

Semiquantitative scattering theory of amorphous materials

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It is argued that the topological disorder in a small region of an amorphous solid can be described by the local strain field related to the local reference crystal. A localized state spread only in one distorted region can be viewed as the consequence of superposition among some Bloch waves and its scattering waves caused by the disorder. A semiclassical approximation is used to calculate the phase shift of Bloch waves in the amorphous solid. The inverse participation ratio and the mobility edge positions in the band tails are formulated in terms of the parameters of the disorder potential. The dependence of the band tail decay rates on static and thermal disorders is derived. The model is applied to *a*-Si, though conceptually it can be implemented to a wide range of disordered systems. The *ab initio* calculations on *a*-Si and the experimental results on *a*-Si:H are compared to the predictions of our model.

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I. INTRODUCTION

The localization of electronic wave function in semiconductors has been intensively studied over nearly 50 years.¹ Most of the studies are based on the multiple-scattering approach due to Anderson. A state is localized in a small region due to the presence of disorder if and only if the probability amplitude of this state in that region remains finite after an infinite time.² Due to the complicated graph summation techniques, the method is difficult to apply to the topological disorder in amorphous systems.³ Though the method is quite general, it doesn't provide a direct link between the key properties, such as the energy dependence of the inverse participation (IPR), the mobility edge position, and the decay rates of the band tails, to the experiments or simulations.

In 1950s, Gubanov *et al.*⁴ suggested that the electronic structure of an amorphous solid could be found by a specially designed perturbation method, in which that of the crystalline counterpart is taken as zero-order approximation. It relates the decay rates of the band tails to the width of the bond-length distribution.⁴ A structural model of an amorphous solid obtained by introducing topological deformation in the reference crystal is also reported.^{5,6} Other theoretical and experimental works also suggest that the gross features of the energy spectrum and the wave functions of amorphous solid are not very different from its crystal counterpart. Hence, for a deeper insight into the electronic structure of the amorphous solid, the energy bands and the Bloch states of the reference crystal (if it exists) can serve as a useful starting point.

Since the disorder potential in amorphous solid is not small, a localized state cannot be obtained from a finite order perturbation theory with a Bloch state as a zero-order solution. On the other hand, semiclassical approximation has been successfully applied to the transport properties in various external fields.⁷ For inhomogeneous static field and/or field of moderate frequency, one can always construct an electronic wave packet so that its size is much smaller than the characteristic length of the external field.⁸ The group velocity \mathbf{v}_{nk}^g of an electron in the *n*th band with wave vector \mathbf{k} is given by⁸

$$\mathbf{v}_{nk}^g = \frac{\partial E_{nk}}{\hbar \partial \mathbf{k}}, \quad (1)$$

and the time evolution of the wave vector \mathbf{k} is

$$\hbar \dot{\mathbf{k}} = e\mathbf{E} + e\mathbf{v} \times \mathbf{B}, \quad (2)$$

where \hbar is Planck's constant, e is the charge of electron, E_{nk} is the dispersion relation of the *n*th band, and \mathbf{E} and \mathbf{B} are the external electric field and magnetic inductions.⁷ The semiclassical approximation does not assume that the external field is small whereas Born approximation requires this.

In this paper, we first illustrate that for a wide class of amorphous solids the disorder in a small region can be described by the atomic displacements relative to a local reference crystal (LRC) of this region. The size of the LRC is determined by the extent of the disorder of the distorted region. In a distorted region, the extra force \mathbf{F} suffered by a Bloch electron χ_{nk} relative to that of LRC is expressed by the atomic displacements relative to the atoms in LRC. In *a*-Si and other amorphous solids, the de Broglie wavelength of valence state or conduction state is shorter than the characteristic length of the disorder potential. The semiclassical approximation⁹ can be used to compute the phase shift of a Bloch state when it passes through a distorted region in an amorphous solid. A simple localization criterion is formulated based on the interference of primary Bloch wave and waves scattered by the disorder potential. By using this criterion, for the first time, we have related important physical quantities such as the positions of mobility edges, the decay rate of band tails, the energy dependence of IPR, etc. to the disorder parameters, the coordination number, and the transition integral. Our predictions are consistent with the available experimental results. We have also performed *ab initio* local density approximation (LDA) (Ref. 10) and tight-binding approximation (TBA) (Refs. 11 and 12) calculations on *a*-Si to verify our results.

II. LOCAL REFERENCE CRYSTAL

For a wide class of amorphous solids, the local coordination is quite similar to that of their crystal counterparts. Thus,

to some extent it is reasonable to characterize the disorder in an amorphous solid by considering the positions of atoms in the amorphous solid as deviations from the positions in the reference crystal, although one cannot assign one reference crystal to a large disorder region as the deviation from the reference crystal increases at larger distances. Hence, to effectively describe the disorder in an amorphous sample, one has to divide the amorphous sample into many small regions and for each small region introduce its own LRC. Such LRCs would be different in their orientations and sizes, which can be determined by the extent of disorder of the corresponding regions in the amorphous solid.

Consider an amorphous solid with only one atom in the primitive cell of its reference crystal. Take a small region in the amorphous solid. One typical lattice site of the LRC of this distorted region is denoted as $\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$, where $\mathbf{n}(n_1 n_2 n_3)$ is the lattice index and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the basis vectors. The positions of $N_1 N_2 N_3$ atoms in the LRC are completely determined by $N_1 N_2 N_3$ groups of numbers $\mathbf{n}(n_1 n_2 n_3)$ $\{n_i = 1, 2, \dots, N_i, i = 1, 2, 3\}$. The positions $\{\mathcal{R}_n\}$ of the atoms in a distorted region are determined by the displacements \mathbf{u}_n of atoms relative to the lattice sites \mathbf{R}_n of its LRC: $\mathcal{R}_n = \mathbf{R}_n + \mathbf{u}_n$. For a given distorted region of an amorphous sample, $\{\mathcal{R}_n\}$ or $\{\mathbf{u}_n\}$ are $N_1 N_2 N_3$ vectors which completely describe the positions of atoms. In current work, the disorder in a distorted region is described by $N_1 N_2 N_3$ given vectors $\{\mathbf{u}_n\}$, eventually by the disorder potential ($V_a - V_c$),

$$V_a(\mathbf{r}) - V_c(\mathbf{r}) \approx \sum_{\mathbf{n}} \sum_{\beta} \frac{\partial U(\mathbf{r} - \mathbf{R}_n)}{\partial R_{n\beta}} \mathbf{u}_{n\beta}, \quad \beta = x, y, z \quad (3)$$

where V_a is the single electron potential of the distorted region, V_c is that of the corresponding LRC, \mathbf{r} is the position vector of electron, and $U(\mathbf{r} - \mathbf{R}_n)$ is the single electron potential for the atom located at \mathbf{R}_n . It is quite direct to write down all the formulae for amorphous solid with several atoms in a primitive cell of its reference crystal.

With a suitable choice of the origin and orientation of the LRC, the atomic displacements in a distorted region relative to its LRC can be made small. For a localized state confined in one distorted region, we may describe it as superposition of a Bloch state with its scattering waves caused by the potential $V_a - V_c$. Argument based on ordinary perturbation or integral equation of scattering supports this point. Although the orientations and/or sizes of local reference crystals may be different, the electronic states and single electron potential V_c are all the same. The difference among different regions in an amorphous sample is reflected in the disorder potential $V_a - V_c$ of each distorted region.

To describe the disorder in a whole amorphous sample, we divide it into many small regions. The disorder in each small region is characterized by a group of displacement vectors $\{\mathbf{u}_n\}$, or in the language of theory of elasticity,¹³ a local strain field referring to its LRC. There exist relative rotations among those distorted regions.¹³ Those relative rotations are global constraints on amorphous structure and prevent it from relaxing to the more stable crystal structure. We will confine ourselves to the localized states spread in only one distorted region of either shorter or longer bond.

We estimate the size of a distorted region which could be described by one reference crystal, in other words the size of a LRC. If the size of a region in an amorphous solid is too large, the atomic displacement in some parts of the region relative to a LRC can be larger than one bond length. Using the atom in the n th cell of LRC as reference will make no difference with using the atom in the $(n+1)$ th cell. The atoms in those parts should be assigned to other LRCs. In *a*-Si,¹⁴ the half width of the bond-length distribution is about 0.2 Å (relative width $\frac{0.2 \text{ \AA}}{2.35 \text{ \AA}}$). Suppose there is no fluctuation in bond angles and dihedral angles, the fastest possible pace to make the absolute displacement of a silicon atom reach standard bond length 2.35 Å is about 12 Si-Si bonds. To keep the deviation in a distorted region from its LRC small, linear size less than 25 Å (including 12 bonds) is safe. Any realistic change in bond length would be alternative after several bonds. The linear size 25 Å is a rather conservative estimation for a distorted region using one LRC. This estimation is supported by a structural study: radial distribution functions of *a*-Ge and *a*-Si calculated on elastically deformed nanocrystals of diameter about 3nm are in good agreement with experiment on amorphous solid.⁶ Such a size of a distorted region is large enough to assure the Bloch states of its LRC is well defined. To understand this point, one can use either of the following two opinions. The LRC itself is infinitely large, only a small part represents the distorted region of amorphous solid. This small part acts as reference to describe the disorder of the region. Another opinion is that for a big sample, zero boundary condition and periodic boundary condition make no difference.¹⁵ Here big means that the number of the atoms on the surface is much smaller than the total number of the atoms in whole cluster.¹⁶

There are six degrees of freedom to choose a LRC: three for the position of origin and three for the orientation. For a distorted region in amorphous solid, a good LRC is the one that minimizes the total deviation from LRC. This can be obtained by a suitable choice of the origin and orientation of the LRC. There could exist several good LRCs for a distorted region in amorphous solid. The best LRC is the one which has the smallest mismatch with its neighboring LRCs. With the conditions (1) minimizing the displacements and (2) the orientation has smallest mismatch with neighboring LRCs, the LRC is unique for a region in amorphous solid. Because we confined our discussion only to the localized states spread in one distorted region, the error caused by different good LRCs which satisfy condition (1) is a higher order small quantity, the main disorder is reflected in Eq. (3). If condition (1) is satisfied, Eq. (3) would be the same for different good LRCs.

III. LOCALIZATION CRITERION

The existence of reference crystal for each small region of an amorphous sample suggests that an electronic state of the amorphous solid could be viewed as a consequence of superposition of some Bloch waves of the reference crystal with their secondary scattering waves caused by the disorder, since the characteristic length of valence states and conduction states are of the order of one bond length (≈ 2.35 Å in

a-Si¹⁴), a distance much shorter than the length scale in which the disorder potential fluctuates obviously.^{14,17} Semiclassical approximation,^{8,9} which requires a small ratio of the de Broglie wavelength to the characteristic length of $(V_a - V_c)$, is justified for computing the phase shift of a Bloch wave produced by disorder. In this approximation, one does not need $(V_a - V_c)/V_c$ to be small.

A. Semiclassical approximation

Suppose a Bloch wave χ_{nk} is scattered by a distorted region \mathcal{D} with a linear size L in an amorphous solid. Similar to Eq. (2), the time evolution of the wave vector of a Bloch wave under the extra force \mathbf{F} of \mathcal{D} relative to its LRC is given by

$$\hbar \dot{\mathbf{k}} = \mathbf{F} = -\nabla(V_a - V_c). \quad (4)$$

Using the primitive cell of LRC numbering the atoms in \mathcal{D} , the x component of extra force suffered by an electron relative to that of LRC is

$$F_x(\mathbf{r}) = \sum_{n\beta} \frac{\partial^2 U(\mathbf{r} - \mathbf{R}_n)}{\partial R_{nx} \partial R_{n\beta}} u_{n\beta}^s, \quad \beta = x, y, z, \quad (5)$$

later its typical value is denoted as F . In current work, the full information of $\{\mathbf{R}_n\}$ and $\{\mathbf{u}_n\}$ is not used. Only the size L of the distorted region along the propagation direction of Bloch wave, typical value of the extra force \mathbf{F} in the distorted region, the width of bond-length distribution, and the width of bond angle distribution are taken as the parameters of disorder. $\{\mathbf{u}_n^s\}$ includes the information of structural correlation. These higher order structural correlations can be only reflected in finer quantity such as the shape of band tails which we will not touch in this work.

B. Localization criterion

A Bloch wave χ_{nk} passes through \mathcal{D} , the phase shift δ_{nk} of scattering wave along some direction is determined by the propagation path L , and the change in wave vector caused by the extra force \mathbf{F} , by means of Eqs. (1) and (4), is

$$\delta_{nk} \sim \frac{FL^2}{|\nabla_{\mathbf{k}} E_{nk}|}. \quad (6)$$

Because we are only concerned about the interference between a Bloch wave and its scattering wave, higher order corrections to the wave function are irrelevant.

If the first coordination shell around an atom is spherically symmetric, the dispersion relation under TBA is¹⁸

$$E_{nk} \sim E_{n0} - zI_n \cos k_x a. \quad (7)$$

Here E_{n0} is the middle of the n th band, z is the coordination number, I_n is the transition integral for the n th band between nearest neighbors, and a is the lattice constant in LRC. If the phase shift δ_{nk} of the secondary scattering wave relative to the primary wave is $\sim \pi$, then outside the distorted region \mathcal{D} , scattering wave will interfere destructively with the primary Bloch state. A localized state is therefore formed inside \mathcal{D}

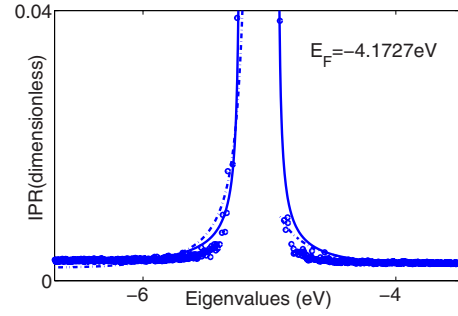


FIG. 1. (Color online) IPR of 512 atom model of *a*-Si dots from *ab initio* calculation (Ref. 10). Dashed line and solid line are from two parameter (FL and zI) least-squares fit and eye guide fit with Eq. (11).

due to the constructive interference of a Bloch state χ_{nk} and its secondary scattering wave.

A more precise dispersion relation than Eq. (7) only complicates formulae and will not lead to any qualitative new feature. In the rest of this paper, we apply above criterion to discuss semiquantitatively some features of the localized states.

C. States close to the bottom or top of a band

Bloch states at the top of valence band and at the bottom of the conduction band are more susceptible to the disorder potential. The former is shorter wave, sensitive to details of atomic displacements of a distorted region. The latter is long wave: a small random potential will easily produce a change in crystal momentum comparable to $\hbar \mathbf{k}$ itself. In other words, states with small group velocity are easily localized. The group velocity of an electron in Bloch state χ_{nk} is $v_{nk}^g \sim \frac{zI_n a}{\hbar} \sin k_x a$; states near to the bottom ($k_x a \sim 0$) and states near to the top ($k_x a \sim \pi$) have smaller v_{nk}^g . According to Eq. (6), they are more easily localized than the states in the middle of a band for a given disorder potential. For k close to $\frac{\pi}{a}$ (the top of valence band), the group velocity of state χ_k^v is $v_k^g = \frac{I_V z}{\hbar} (\frac{E_t - E}{I_V z})^{1/2}$, where $E_t = E_0^V + zI_V$ is the top of the valence band, and I_V is the transition integral for valence band. By Eq. (6), for a valence state χ_k^v with energy E_k , the change in phase shift with energy is given by $\frac{d\delta_k}{dE} = \frac{FL^2}{a(E_t - E_k)^{3/2} (I_V z)^{1/2}}$. For a given distorted region with short bonds, Bloch states close to E_t will suffer larger phase shift. They are more readily localized than the states in the middle of the band. Similar conclusion holds for the Bloch states in the bottom of conduction band. In Fig. 1 the IPR is plotted against electron energy for a model of *a*-Si. Large IPR appears at the top and bottom of a band, in agreement with the above prediction.

D. Location of the mobility edge

The upper mobility edge of the valence band is the deepest energy level $E_{k_*}^V$ that the largest distorted region could localize, i.e., produces a phase shift π for the corresponding Bloch state. This leads to a specific wave vector k_*^V (the deepest one, i.e., mobility edge) which satisfies $\sin k_*^V a$

$= \frac{FL^2}{z_V I_V a \pi}$ in TBA. The energy difference between the top of crystalline valence band and the mobility edge is E_{me}^V
 $= z_V I_V \{1 - [1 - (\frac{FL^2}{z_V I_V a \pi})^2]^{1/2}\} \sim \frac{(FL^2)^2}{z_V I_V}$, last \sim only holds for $\frac{FL^2}{z_V I_V a \pi} \ll 1$. It is obvious that stronger disorder potential and narrower band lead to a deeper mobility edge. The lower mobility edge of the conduction band can be obtained similarly. The energy difference Δ_m between the lower mobility edge of the conduction band and the upper edge of the valence band is

$$\Delta_m \approx G^C + \left[\frac{\left(\frac{FL^2}{a\pi}\right)^2}{z_V I_V} + \frac{\left(\frac{F_C L_C^2}{a\pi}\right)^2}{z_C I_C} \right], \quad (8)$$

where G^C is the band gap of LRC, F_C is the typical values of extra force of long bond region, and L_C is the linear size of the long bond region. Because the van Hove singularity is smeared out by the disorder, gap in amorphous solid is ambiguous. Δ_m can be defined in a simulation by identifying two mobility edge states from IPR.

In TBA, the middle of a band $k_x a = \frac{\pi}{2}$, the group velocity reaches its maximum $\frac{z_n a}{\hbar}$. By Eq. (6), to localize the states in the middle of the n th band, we need $\frac{FL}{z_n a} \gtrsim \pi$ (simulation shows $\frac{L}{a} \sim 3$ in the 64 atom a -Si model¹⁴). States in the middle of a band are most difficult to localize. If those states are localized, the whole band is localized. A stronger localization condition is $\Delta k \sim k$. In the middle of band $k_x = \frac{\pi}{2a}$, the change in wave vector is $\frac{FL}{z_n a}$. It leads to the condition to localize whole band $\frac{FL}{z_n} \gtrsim \frac{\pi}{2}$. This value is too small comparing with previous works¹⁹ based on multiple-scattering method $\frac{FL}{z_n} \sim 6-34$. The deeper localized states are generated by the deeper Bloch states and are spread in several distorted regions (shorter-long-short-...). Current method only considers the states localized in one distorted region. One cannot expect a better estimate.

E. Energy dependence of inverse participation ratio

The IPR \mathcal{I}_j of a localized eigenstate ψ_j could be approximated as $\mathcal{I}_j \sim \frac{a^3}{\xi_j^3}$, where ξ_j is the localization length of ψ_j . If a Bloch wave χ_{nk} suffers a phase shift π by some distorted region to produce ψ_j , it is localized in range ξ_j : $\xi_j \Delta k \sim \pi$. The change in wave vector is $\Delta \mathbf{k} \sim \frac{FL}{\nabla_{\mathbf{k}} E_k}$,

$$\xi_j \sim \frac{\pi}{\Delta k} = \frac{\pi \nabla_{\mathbf{k}} E_k}{FL} \sim \frac{\pi z I_n a \sin ka}{FL}. \quad (9)$$

According to Eq. (5), the extra force $F \sim \epsilon$, where ϵ is the relative change in lattice constant. To minimize the free energy, a denser region with shorter bonds and small angles will gradually decay away toward the mean density rather than exhibit an abrupt transit to a diluter region and vice versa. Therefore the size L of a denser region is proportional to ϵ . Equation (9) indicates $\xi \sim \frac{a}{2}$; this agrees with the result of the deformed coordinate method.⁴ The advantage of Eq. (9) is that it also reveals the role of the coordination number z and the transition integral I . The dependence on \mathbf{k} (wave-

length and propagation direction of Bloch wave) is displayed too in Eq. (9): close to band edge, $ka \sim 0$ or $\frac{\pi}{a}$, the localization length is small, and IPR is high (see Fig. 1).

Making use of Eqs. (9) and (7),

$$\xi_j(E_{kj}) = \frac{\pi z I_V a}{FL} \left[1 - \left(\frac{E_{kj} - b_{me}^V + z I_V - E_{me}^V}{I_V z} \right)^2 \right]^{1/2}, \quad (10)$$

b_{me}^V is the location of the upper mobility edge of valence band. When we approach b_{me}^V from the upper side with higher energy, it is easy to find $\xi_j \rightarrow L$ from Eq. (10), localization length ξ approaches to the size L of whole region as $(E_{kj} - b_{me}^V)^\alpha$, where $\frac{1}{2} < \alpha < 1$, and it is close to the lower bound of previous works.²⁰ The trend expressed by Eq. (10) is consistent with a simulation based upon time-dependent Schrodinger equation.²¹

For a localized state derived from Bloch wave χ_{kj}^V , the energy dependence of IPR can be found

$$\mathcal{I}(E_{kj}) \sim \frac{(FL/\pi z I_V)^3}{\left[1 - \left(\frac{E_{kj} - E_0^V}{z I_V} \right)^2 \right]^{3/2}}. \quad (11)$$

This is a prediction of our work. Equations (10) and (11) are not quite satisfied because E_{kj} is the corresponding energy level in LRC, not the eigenvalue of the localized state ψ_j . It can be cured by taking into account energy-level shift caused by the disorder. Figure 1 shows IPR vs eigenvalues in a 512 atom model of a -Si.¹⁴ As expected from Eq. (11), IPR decreases from higher values at band edges to smaller values in the band interior. The functional form (11) fits the simulation quite well.

According to Eq. (11), the least squares fitting parameters in Fig. 1 are $(FL)_V = 1.256$ eV, $(zI)_V = 3.185$ eV, $E_0^V = -7.390$ eV, $(FL)_C = 1.437$ eV, $(zI)_C = 3.502$ eV, and $E_0^C = -1.080$ eV. The width of valence band of c -Si is about 2.7eV and the width of conduction band is²² about 2.3eV. The fit parameters are reasonable, something like what we expected for Si. Gap for c -Si is²² 1.12eV, substitute above parameters into Eq. (8), and the distance between mobility edges is 2.205eV. It falls in the range 1.58–2.43 eV of the observed optical gap.^{23–25}

The aim of this work is to use crystalline parameters such as transition integral, coordination number, and disorder parameters of amorphous solid to compute some features of the localized states. From the bond-length distribution and the bond angle distribution of an amorphous solid, the extra force F and the linear size L of a denser or diluter region can be estimated. Since the fitting parameter of the band width is not far from the realistic crystalline band width, a direct computation will give a reasonable IPR curve and a sensible value of the distance between two mobility edges.

F. Decay rate of the band tails

In a distorted region of a -Si where bonds are shortened, valence states have more amplitude in the middle of bonds. The disorder potential is important only in the middle of bonds rather than close to the core of atoms. Electrons will

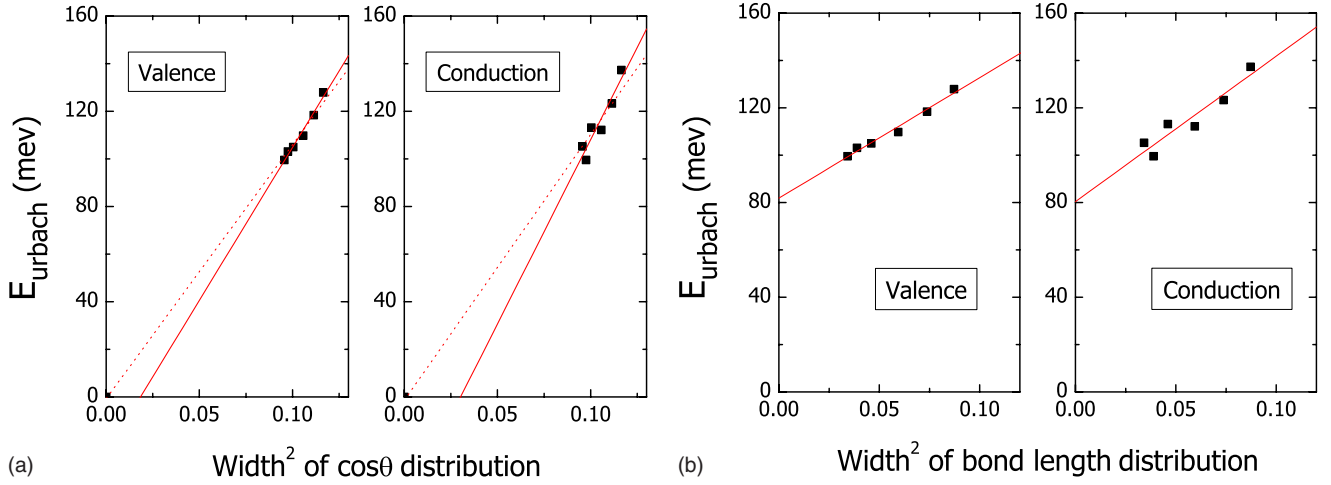


FIG. 2. (Color online) Left: E_U^V and E_U^C vs $\sigma_{\cos \theta}^2$. Six squares are extracted from the density of states of six models computed in TBA, dotted line and solid lines are least square fits with and without (0,0) points. Right: E_U^V and E_U^C vs σ_{BL}^2 .

feel $V_a - V_c$ more than a region where bonds are closer to normal. Valence tail states are easily localized in a distorted region with shorter bonds.^{14,26} On the other hand, in a distorted region with longer bonds, the conduction levels are lowered and the probability of conduction electrons staying in the middle of nearest-neighbor atoms becomes larger than a region where bonds are closer to the mean. The conduction tail states are more readily localized in a distorted region with longer bonds and large angles.^{14,26}

The effect of three- and four-point atomic correlations on the shape of band tail is subtle: localized states adhere to one-dimensional (1D) filaments in amorphous solid.¹⁷ According to the theory of line shape,²⁷ the decay rate $E_U^{V(C)}$ of valence (conduction) tail can be derived from the relative shift of energy levels of LRC caused by disorder. Suppose Δb is the width of the bond-length distribution, the blurring δk in wave vector k is $\frac{\Delta b}{b}k$, where b is the average bond length. The shift of level E_k^v (E_k^c) for a Bloch state χ_k^v (χ_k^c) in valence (conduction) band by the disorder is in $\Delta E_k^{v(c)} = \int d\tau (V_a - V_c) |\chi_k^{v(c)}|^2$. The relative level shift due to this bond-length distribution is $\delta k \frac{d}{dk} \Delta E_k^c$. It is easy to see $V_a - V_c \propto \frac{\Delta b}{b} V_c$. Then

$$E_U^{V(C)} \sim \frac{\Delta b}{b} k \frac{1}{k} \frac{\Delta b}{b} V_c = \left(\frac{\Delta b}{b} \right)^2 |V_c| = \frac{\left(\frac{\Delta b}{b} |V_c| \right)^2}{|V_c|}. \quad (12)$$

If we make a correspondence between the structural disorder $\frac{\Delta b}{b} |V_c|$ and on-site spread W of levels, Eq. (12) is comparable to the results of the models of on-site disorder $E_U \sim 0.5 \frac{W^2}{B}$ (B is the band width²⁸) and $E_U \sim \frac{\pi}{4} \frac{W^2}{3\pi^2 \frac{\hbar^2}{2ml^2}}$, where l and W are correlation length and variance of random potential.²⁹ Equation (12) is also consistent with an assumption made by Cody *et al.*³⁰ to explain their absorption edge data in a -Si:H. Since the width of the bond-length distribution is $\frac{\Delta b}{b} \approx 0.1$ and $|V_c| \sim 1-10$ eV, the order of magnitude of mobility edge should be $\left(\frac{\Delta b}{b} |V_c| \right)$, several tenths of eV to 1eV, so that the decay rate $E_U^{V(C)}$ of band tails is around several tens to several

hundred meV. Both estimates agree with experimental observations.³¹ Equation (12) indicates that $E_U^{V(C)}$ is proportional to static disorder that is characterized by $\left(\frac{\Delta b}{b} \right)^2$, in consistent with the fact that $E_U^{V(C)}$ of a -Si:H increases with deposition power.³¹ Δb and b could also be explained as the width and the average value of the bond angle distribution.

Since local compression is compensated by adjacent local tensile in any realistic amorphous solids, $E_U^V \sim \frac{\varsigma^V}{\varsigma^C} E_U^C$, where ς^V (ς^C) is an order one dimensionless constant characterizing the peak (node) of valence (conduction) states. In a -Si and a -Si:H, disorder potential ($V_a - V_c$) takes larger value in the middle of Si-Si bonds. Since valence states are more in the middle of bonds than conduction states,³² they feel the distortion more. Therefore $\varsigma^V > \varsigma^C$. One expects $E_U^V > E_U^C$. This agrees with measurements in a -Si:H: $E_U^V \sim 43-103$ meV vs $E_U^C \sim 27-37$ meV, linear relation among E_U^V and E_U^C has also been observed.³¹

To test the correctness of Eq. (12), for six a -Si models with 20 000 atoms, we undertook a TBA calculation on density of states.^{11,12,33} $E_U^{V(C)}$, the width $\sigma_{\cos \theta}$ of bond angle distributions, and the width σ_{BL} of the bond-length distribution are extracted for each model. The left panel of Fig. 2 clearly shows good linear relation between E_U^V (E_U^C) and $\sigma_{\cos \theta}^2$ curves pass origin (decay rate $E_U^{V(C)}$ is zero for crystal due to van Hove singularity) as displayed in Eq. (12). Equation (12) should be further tested in ion implanted samples, where a continuous increase in disorder from crystal to amorphous is realized by increasing the dose.³⁴ The E_U^V (E_U^C) vs σ_{BL}^2 curve does not pass origin (see the right panel of Fig. 2), this is an indication that the bond angle disorder is a little more decisive in determining the shape of a band tail than the bond-length disorder for a well-relaxed structure.^{14,26}

The electron-phonon interaction is strong in amorphous solid.³⁵ At finite temperature, the displacement of an atom in amorphous solid from the corresponding position in the LRC at zero temperature is a vector sum of the static displacement \mathbf{u}_s and thermal vibration displacement $\mathbf{u}_T(t)$ from the zero-temperature configuration of amorphous solid, where t is the time moment. In ordinary optical-absorption experiment, time interval T is much longer than the period of the slowest

mode, therefore the observed decay rate of conduction-band tail is a time average $\overline{E_U^C} = \frac{1}{T} \int_0^T dt \varsigma^C (\frac{\mathbf{u}_s + \mathbf{u}_T(t)}{a})^2 |V_c|$. Atoms vibrate around their equilibrium positions in amorphous solid and the time average of the cross term $\mathbf{u}_s \cdot \mathbf{u}_T(t)$ is zero. Thus decay rate from static disorder and the decay rate from thermal disorder is additive³⁰ $\overline{E_U^C} = E_{U_s}^C + E_{U_T}^C$, where the static part $E_{U_s}^C = \varsigma^C (\frac{u_s}{a})^2 |V_c|$. Thermal part is given by a similar expression $E_{U_T}^C = \varsigma^C (\overline{\mathbf{u}_T^2} / a^2) |V_c|$, where $\overline{\mathbf{u}_T^2} = \frac{1}{T} \int_0^T dt [\mathbf{u}_T(t)]^2$ is the long-time average of the square of amplitude of vibration. An ultrafast probe of absorption edge may find the oscillation in $\overline{E_U^C}$. Since $\overline{\mathbf{u}_T^2} \propto \frac{k_B T}{B_C} a^2$, where B_C is typical binding energy in the diluter regions where conduction tail states are localized.¹⁸ $\overline{E_U^C}$ linearly increases with temperature, $E_{U_T}^C = \varsigma^C k_B T \frac{|V_c|}{B_C}$. Similarly, the result holds for $\overline{E_U^V}$. The is consistency with the fact that above 350 K absorption edge linearly increases with $k_B T$ in *a*-Si:H.^{36,37} Because $B_V > B_C$, E_U^C is more susceptible to the thermal disorder³⁸ than E_U^V , as observed in Ref. 37.

IV. SUMMARY

Two major assumptions of this work are (1) the existence of local reference crystals for amorphous solid and (2) semiclassical approximation. For a wide class of amorphous solids with topological disorder, by viewing an amorphous solid as many distorted regions relative to corresponding LRCs, we push forward some understandings on the localized states confined in one distorted region. The predicted energy dependence of IPR, the distance between two mobility edges, and the dependence on static disorder and on thermal disorder of the decay rate of band tails agree with available experiments and simulations. We explained the fact that va-

lence tail states are more localized in a denser region with smaller bond angles and shorter bond lengths and conduction tail states are more localized in diluter region with longer bond lengths and larger bond angles in *a*-Si.^{14,26}

The present work is inapplicable to amorphous solid for which the reference crystal does not exist. In principle for each crystal, there exists an amorphous solid for which the local coordination is similar to that of the crystal. The inverse is not true. In an amorphous solid, atoms fill space without the requirement of translational invariance. There are more types of amorphous solids than those of crystals. For some amorphous solids, it is quite possible that we cannot find a similar crystal structure as reference. For those amorphous solids, current model is not applicable. Given an arbitrary set of atomic positions $\{\mathcal{R}_n\}$, correlated or random, Anderson's multiple-scattering consideration can be used, which does not need Bloch wave as starting point.

In this work, we left many important questions untouched: the justification of Eq. (4) in the same footing as Eq. (2), localized states spread in several distorted regions, the consequence of higher order atomic correlations, the origin of exponential shape of band tails, the origin and thermodynamic consequence of the relative rotation among distorted regions, etc. We will address some of them in an upcoming paper.³⁹

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¹B. Kramer and A. MacKinnon, Rep. Prog. Phys. **56**, 1469 (1993).

²P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

³P. W. Anderson, Proc. Natl. Acad. Sci. U.S.A. **69**, 1097 (1972).

⁴For review, see K. Moorjani and C. Feldman, Rev. Mod. Phys. **36**, 1042 (1964).

⁵F. Yonezawa and J. L. Birman, Phys. Rev. B **16**, 2707 (1977).

⁶J. K. Bording and J. Taftø, Phys. Scr. **62**, 499 (2000).

⁷I. M. Lifshits, M. Ya. Azbel, and M. I. Kaganov, *Electron Theory of Metals* (Consultants Bureau, New York, 1973).

⁸N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1976).

⁹A. B. Pippard, *Dynamics of Conduction Electrons* (Gordon and Breach, New York, 1965).

¹⁰E. Artacho, E. Anglada, O. Dieguez, J. D. Gale, A. Garcia, J. Junquera, R. M. Martin, P. Ordejon, J. M. Pruneda, D. Sanchez-Portal, and J. M. Soler, J. Phys.: Condens. Matter **20**, 064208 (2008); Siesta on *a*-Si-512 with single zeta polarized basis sets

(SZP: 1 function for 3*s*, 3 for 3*p*, and 5 for 3*d*).

¹¹D. A. Drabold and O. F. Sankey, Phys. Rev. Lett. **70**, 3631 (1993).

¹²J. J. Ludlam, S. N. Taraskin, S. R. Elliott, and D. A. Drabold, J. Phys.: Condens. Matter **17**, L321 (2005).

¹³A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity*, 4th ed. (Cambridge University Press, Cambridge, 1927).

¹⁴Y. Pan, M. Zhang, and D. A. Drabold, J. Non-Cryst. Solids **354**, 3480 (2008).

¹⁵W. J. Swiatecki, Proc. Phys. Soc., London, Sect. A **64**, 226 (1951).

¹⁶R. Peierls, Proc. Natl. Inst. Sci. India, Part A **20**, 121 (1954); see also R. Peierls, in *Surprises in Theoretical Physics* (Princeton University, New Jersey, 1979), pp. 64–73.

¹⁷Y. Pan, F. Inam, M. Zhang, and D. A. Drabold, Phys. Rev. Lett. **100**, 206403 (2008).

¹⁸J. Callaway, *Quantum Theory of the Solid State* (Academic, London, 1974).

¹⁹V. Srivastava, J. Phys.: Condens. Matter **1**, 4311 (1989).

²⁰N. F. Mott, *Conduction in Non-Crystalline Materials*, 2nd ed. (Oxford University Press, Oxford, 1993).

²¹H. De Raedt and P. De Vries, Z. Phys. B: Condens. Matter **77**,

- 243 (1989).
- ²²B. V. Zeghbroeck, Chap. 2, 2007 (<http://ece-www.colorado.edu/bart/book>).
- ²³A. Deneuve, A. Mini, and J. C. Bruyere, *J. Phys. C* **14**, 4531 (1981).
- ²⁴A. O. Kodolbas, *Mater. Sci. Eng.*, B **98**, 161 (2003).
- ²⁵K. Haga, K. Yamamoto, M. Kumano, and H. Watanabe, *Jpn. J. Appl. Phys.*, Part 2 **25**, L39 (1986).
- ²⁶J. Dong and D. A. Drabold, *Phys. Rev. Lett.* **80**, 1928 (1998).
- ²⁷For example, A. M. Stoneham, *Rev. Mod. Phys.* **41**, 82 (1969).
- ²⁸S. Abe and Y. Toyozawa, *J. Phys. Soc. Jpn.* **50**, 2185 (1981).
- ²⁹C. M. Soukoulis, M. H. Cohen, and E. N. Economou, *Phys. Rev. Lett.* **53**, 616 (1984).
- ³⁰G. D. Cody, T. Tiedje, B. Abeles, B. Brooks, and Y. Goldstein, *Phys. Rev. Lett.* **47**, 1480 (1981).
- ³¹S. Sherman, S. Wagner, and R. A. Gottscho, *Appl. Phys. Lett.* **69**, 3242 (1996).
- ³²W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
- ³³N. Mousseau and G. T. Barkema, *Phys. Rev. B* **61**, 1898 (2000).
- ³⁴For example, S. Sorieul, J.-M. Costantini, L. Gosmain, G. Calas, J.-J. Grob, and L. Thomé, *J. Phys.: Condens. Matter* **18**, 8493 (2006).
- ³⁵R. Atta-Fynn, P. Biswas, and D. A. Drabold, *Phys. Rev. B* **69**, 245204 (2004).
- ³⁶G. Weiser and H. Mell, *J. Non-Cryst. Solids* **114**, 298 (1989).
- ³⁷S. Aljishi, J. D. Cohen, S. Jin, and L. Ley, *Phys. Rev. Lett.* **64**, 2811 (1990).
- ³⁸D. A. Drabold and P. A. Fedders, *Phys. Rev. B* **60**, R721 (1999).
- ³⁹M.-L. Zhang and D. A. Drabold (unpublished).