A semi-quantitative scattering theory of amorphous materials

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Abstract

It is argued that topological disorder in amorphous solids can be described by local strains related to local reference crystals and local rotations. An intuitive localization criterion is formulated from this point of view. The Inverse Participation Ratio and the location of mobility edges in band tails is directly related to the character of the disorder potential in amorphous solid, the coordination number, the transition integral and the nodes of wave functions of the corresponding reference crystal. The dependence of the decay rate of band tails on temperature and static disorder are derived. Ab initio simulations on a-Si and experiments on a-Si:H are compared to these predictions.

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Electronic localization induced by diagonal disorder or by structural disorder has been intensively studied over nearly fifty years\cite{1}. However, key properties like the energy dependence of the Inverse Participation Ratio (IPR), the location of the mobility edges and the decay rate of and tails are expressed in an obscure way, not directly accessible to experiment or simulation\cite{2}. Perturbation theory has been applied to approximate the electron states of amorphous solids (AS), starting with a crystalline counterpart as zero order solution\cite{3} even before Anderson’s classical work\cite{2}. In this Letter we suggest that a local formulation of perturbation theory is effective for the localized states confined to one distorted region and for the first time relate important physical quantities such as the decay rate of band tails and energy dependence of IPR etc. to basic material properties.

Similar to the theory of elasticity\cite{4}, the distorted regions in AS can be characterized by local strains referring to their local reference crystal (LRC) and local rotations. By a suitable choice of origin and orientation of LRC, the atomic displacements of a distorted region of AS relative to its LRC are small. Thus the relative change in potential energy for each distorted region in AS is small. Perturbation theory is justified for each distorted region. The semi-classical approximation (SCA)\cite{5} can further simplify the calculation of scattering waves caused by a distorted region, since the de Broglie wavelength for low-lying excitations is of order one bond length ($\approx 2.35$ Å in a-Si\cite{6}), a distance much shorter than the characteristic range in which the random potential fluctuates\cite{7,8}. The motion of electronic packet under extra force of AS relative to LRC can be described by the Ehrenfest theorem\cite{5}.

We first formulate an intuitive localization criterion for the states confined to one distorted region. Then the IPR, the position of mobility edge and Urbach energy are related to the distortion relative to the LRC, the coordination number and the inter-cell transition integral. The predictions are consistent with available experiments. We also performed \textit{ab initio} local density approximation (LDA)\cite{9} and tight binding approximation (TBA)\cite{10,11} computations on a-Si to verify our results.

Consider a distorted region $D$, with linear size $L$. Using the primitive cell of LRC numbering the atoms in $D$, the x-component of extra force suffered by an electron relative to that of LRC is

$$F_x(r) = \sum_{n,\beta} \frac{\partial^2 U(r - R_n)}{\partial R_{nx} \partial R_{n\beta}} u_{n\beta}, \quad \beta = x, y, z$$ \hspace{1cm} (1)

later its characteristic value of is denoted as $F$. $n$ is lattice index, $R_n$ and $u_{n\beta}$ are the
position vector and the $\beta$th component of the static displacement of the atom $n$ respectively. $U(r - R_n)$ is the potential energy felt by an electron at $r$ from the atom at $R_n$.

A Bloch wave $\psi_{nk}^c$ of LRC passes through $D$, and in SCA, the change in the $x$ component of the wave vector after scattering is

$$\Delta k_x \sim \frac{(FL)_x}{\nabla k_x E_{nk}}$$

(2)

$FL$ measures the magnitude of random potential in $D$. The phase shift $\delta_{nk}$ of state $\psi_{nk}^c$ is determined by the change in momentum and the propagation path of the Bloch wave

$$\delta_{nk} \sim \frac{FL^2}{|\nabla k E_{nk}|}$$

(3)

where $E_{nk}$ is dispersion relation of the $n$th energy band of the LRC. $FL^2$ is the strength of a potential well (the product of the depth of potential well and the range of force) in standard scattering theory. If the first coordination shell around an atom is spherically symmetric, the dispersion relation in TBA is

$$E_{nk} \sim E_{n0} - z I_n \cos k_x a.$$  

(4)

Here $E_{n0}$ is the middle of the $n$th band ($k_x a = \pi/2$), $z$ is the coordination number of a cell, $I_n$ is the transition integral for the $n$th band, $a$ is the lattice constant in LRC. For a semi-quantitative discussion, crude dispersion relation will not invalidate essential points. If the phase shift $\delta_{nk}$ of the secondary scattering waves relative to the primary wave is $\sim \pi$, then outside $D$, scattering waves will interfere destructively with the primary Bloch state. No probability amplitude appears outside $D$. A localized state is therefore formed inside $D$ due to the constructive interference of a Bloch state $\psi_{nk}^c$ and its secondary scattering waves.

Bloch states of LRC at top of valence and at bottom of the conduction edges are susceptible to the random 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 momentum comparable to $\hbar k$ itself. In other words, states with small group velocity are easily localized. The group velocity of an electron in state $\psi_{nk}^c$ in TBA is $v_{nk}^g \sim \frac{z I_n}{a} \sin k_x a$, states near to bottom ($k_x a \sim 0$) and states near to top ($k_x a \sim \pi$) have small $v_{nk}^g$. According to Eq.(3), they are more easily localized than the states in the middle of a band for a given random potential. For $k$ close to $\frac{\pi}{a}$, with TBA dispersion
The upper mobility edge of the valence band is the deepest energy level \( E_{V, n} \), that the largest distorted region could localize, i.e. produce a phase shift \( \pi \) for the corresponding Bloch state. In TBA, this leads to \( \sin k_V^* a = \frac{F_L^2}{z I_V a \pi} \). The energy difference between the top of a band and the mobility edge is \( E_{V, me} = z I_V V^* \left\{ 1 - \left[ 1 - \left( \frac{F_L^2}{z I_V a \pi} \right)^2 \right]^{1/2} \right\} \sim \left( \frac{F_L^2}{z I_V a \pi} \right)^2 \), last \( \sim \) only holds for \( \frac{F_L^2}{z I_V a \pi} \ll 1 \). It is obvious that stronger random 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 \( \Delta_m \) between the lower mobility edge of the conduction band and the upper edge of the valence band is

\[
\Delta_m \approx G^C + \left[ \frac{(F_L^2 a \pi)^2}{z I_V IV^*} + \frac{(F_C L^2 a \pi)^2}{z C IC^*} \right]
\]

(5)

where \( G^C \) is the band gap of LRC. Because the van Hove singularity is smeared out in AS, gap in amorphous solid is ambiguous. \( \Delta_m \) can be defined in a simulation by identifying two edge states.

In the middle of a band \( k_x a = \frac{\pi}{2} \), the group velocity reaches its maximum \( \frac{2 I_n a}{\hbar} \). By Eq. (3), to localize the states in the middle of the \( n \)th band, we need \( \frac{F_L L}{z I_n a} \gtrsim \pi \). 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 \( k_x = \frac{\pi}{2} a \), by Eq. (2) the change in wave vector is \( \frac{FL}{z I_n} \). It leads to the condition to localize a whole band \( \frac{F_L}{z I_n} \gtrsim \frac{\pi}{2} \) (smaller than \( \frac{F_L}{z I_n} \sim 6 - 34 \)\( \frac{13}{13} \)). The deeper localized states in AS are generated by the deeper Bloch states of LRC, are spread in several distorted regions. Because current local description only considers the states localized in one distorted region, we cannot expect a better estimate.

The IPR \( I_j \) of a localized eigenstate \( \psi_j \) could be approximated as \( I_j \sim \frac{a^3}{\xi_j^3} \), \( \xi_j \) is the localization length of \( \psi_j \). If a Bloch wave \( \psi_{nk}^c \) suffers a phase shift \( \pi \) by some distorted region to produce \( \psi_j \), it is localized in range \( \xi_j : \xi_j \Delta k \sim \pi \). The change in wave vector is
$\Delta k \sim \frac{F L}{V_k E_k}$,

$$\xi_j \sim \frac{\pi}{\Delta k} = \frac{\pi \nabla_k E_k}{F L} \sim \frac{\pi z I a \sin ka}{F L}$$  \hspace{1cm} (6)

($\sim$ is obtained under TBA). According to Eq. (6), $F \sim \epsilon$, $\epsilon$ 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 distorted region is proportional to $\epsilon$. Eq. (6) indicates $\xi \sim \frac{a}{\epsilon^2}$ [3]. The advantage of Eq. (6) is that it reveals the role of the coordination number $z$ and the transition integral $I$. The dependence on $k$ (wave length and propagation direction of Bloch wave) is also displayed in Eq. (6): close to band edge of LRC, $ka \sim 0$ or $\pi a$, the localization length is small and IPR is high (see Fig. 1).

Making use of Eqs. (6) and (4),

$$\xi_j(E_{k^j}) = \frac{\pi z I a}{F L} \left[1 - \left(\frac{E_{k^j} - b_{me}^V + z I V - E_{me}^V}{z I z}ight)^2\right]^{1/2}$$ \hspace{1cm} (7)

$b_{me}^V$ is the location of the 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. (7), localization length $\xi$ approach to the size $L$ of whole sample as $(E_{k^j} - b_{me}^V)^\alpha$, where $\frac{1}{2} < \alpha < 1$, it is close the lower bound of previous works [14]. The trend expressed by (7) is consistent with a simulation based upon time-dependent Schrodinger equation [15].

For a localized state derived from Bloch wave $\psi_{k^j}^c$ in LRC, the energy dependence of IPR can be found

$$I(E_{k^j}) \sim \frac{(F L / \pi z I V)^3}{\left[1 - \left(\frac{E_{k^j} - E_0^V}{z I V}\right)^2\right]^{3/2}}$$ \hspace{1cm} (8)

This is a new prediction of our work. Eqs. (7) and (8) are not quite satisfied because $E_{k^j}$ is the corresponding energy level in LRC, not the eigenvalue of the localized state $\psi_{k^j}^a$. It can be cured by taking into account energy level shift caused by the disorder in AS relative to LRC. Fig. 1 shows IPR vs. eigenvalues in a 512-atom model of a-Si [7]. As expected from Eq. (8), IPR decreases from highest values at band edges to small values in the band interior. The functional form (8) fits the simulation rather well.

According to Eq. (8), the least squares fitting parameters in Fig. 1 are $(F L)_V = 1.256 eV$, $(z I)_V = 3.185 eV$, $E_0^V = -7.390 eV$, $(F L)_C = 1.437 eV$, $(z I)_C = 3.502 eV$, $E_0^C = -1.080 eV$. The width of valence band of c-Si is about 2.7 eV, the width of conduction band is about 2.3 eV [16]. The fit parameters are reasonable something like what we expect for Si. Gap for
c-Si is 1.12 eV [16], using above parameters with help of Eq. (5), the distance between mobility edges is 2.205 eV. Result from LRC model falls in the range 1.58-2.43 eV of the observed optical gap [17, 18, 19].

In a distorted region of a-Si where bonds are shortened, valence states have more amplitude in the middle of bonds. Random potential $V_a - V_c$ (the difference between the amorphous and crystalline potentials) is important only in the middle of bonds rather than close to the core of atoms. Electrons will feel $V_a - V_c$ more than a region where bonds more close normal. Valence tail states are easily localized in a distorted region with shorter bonds [7, 20]. 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. Conduction tail states are more readily localized in a distorted region with longer bonds and large angles [7, 20].

The effect of three- and four- point correlation on the shape of band tail is subtle: localized states adhere to 1D filaments in AS network [8]. In the spirit of scattering theory of line shape [21], the decay rate $E_U^{V(C)}$ of valence (conduction) tail can be derived from the relative shift of energy levels of LRC. Suppose $\Delta b$ is the distribution width of bond length (BL), the blurring $\delta k$ in wave vector $k$ is $\frac{\Delta b}{b} k$. The shift of level $E_k^v$ ($E_k^c$) for a Bloch state $\psi_k^v$ ($\psi_k^c$) in valence (conduction) band by the disorder in AS is $\Delta E_k^{v(c)} = \int d\tau (V_a - V_c) |\psi_k^{v(c)}|^2$. The relative level shift due to this BL distribution is $\delta k \frac{2}{dk} \Delta E_k^c$. It is easy to see $V_a - V_c \propto \frac{\Delta b}{a} V_c$. Then

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

(9)

If we make a correspondence between structural disorder $\frac{\Delta b}{b} |V_c|$ and on-site spread $W$ of
levels, Eq. (9) is comparable to \( E_U \sim 0.5 \frac{W^2}{B} \) \( (B \) is the band width \) \cite{22}, and \( E_U \sim \frac{\pi}{4} \frac{W^2}{B^2} \) \( \frac{\text{meV}}{\text{meV}} \) \cite{23}, where \( L \) and \( W \) are correlation length and variance of random potential. Eq. (9) is also consistent with an assumption of Cody et. al. to explain their absorption edge data in a-Si:H \cite{24}. Since the width of BL distribution is \( \Delta b_b \approx 0.1 \) and \( |V_c| \sim 1 - 10 \text{eV} \), the width of mobility edge should be \( (\Delta b_b)|V_c| \), several tenth eV to 1eV, so that the decay rate of band tails is around several tens to several hundred meV. Both agree with experimental observations \cite{25}. Eq. (9) indicates \( E^{(C)}_V \) is proportional to static disorder that is characterized by \( (\Delta b_b)^2 \), in consistent with the fact that \( E^{(C)}_V \) of a-Si:H increased with deposition power \cite{25}. \( \Delta b \) and \( b \) could also be explained as the width and the average value of BA distribution.

Because local compression is compensated by adjacent local tensile in AS, \( E_U^{(V)} \sim \frac{\zeta_v}{\zeta_c} E^{(C)}_U \), where \( \zeta_v \) \( (\zeta_c) \) is an order one dimensionless constant characterizing the peak (node) of valence (conduction) states. In a-Si and a-Si:H, random potential \( (V_a - V_c) \) has larger distortion in the middle of Si-Si bonds, since valence states are more in the middle of bonds than conduction states \cite{6}, they feel the distortion more. Therefore \( \zeta_v > \zeta_c \). One expect \( E^{(V)}_U > E^{(C)}_U \). This agrees with measurements in a-Si:H: \( E^{(V)}_U \sim 43-103 \text{meV} \) vs. \( E^{(C)}_V \sim 27-37 \text{meV} \), linear relation among \( E^{(V)}_U \) and \( E^{(C)}_U \) has also been observed \cite{25}.

\[ E^{(V)}_U \text{ and } E^{(C)}_U \text{ vs. } \sigma^2_{\cos \theta}: 6 \text{ squares are extracted from TBA, dotted line and solid line are least square fits with and without (0,0) points.} \]

To test correctness of Eq. (9), we undertook a TBA calculation for DOS of six a-Si models with 20,000 atoms \cite{10, 11, 26}. \( E^{(C)}_U \), the width \( \sigma_{\cos \theta} \) of BA distributions and the width \( \Delta b \)
of BL distribution are extracted. Fig 2 clearly shows good linear relation between $E_U^V$ ($E_U^C$) and $\sigma^2\cos\theta$, curves pass origin ($E_U^{V(C)}$ is zero for crystal) as displayed in Eq. (9). It can be further tested in ion implanted samples, where a continuous increase disorder from crystal to amorphous are realized by increasing the dose [27]. The $E_U^V$ ($E_U^C$) vs. $(\Delta b)^2$ curve does not pass origin (not showing here), this is an indication that BA disorder is a little more decisive in determine the shape of a band tail than BL disorder for a well relaxed structure [7, 20].

The electron-phonon interaction is strong in AS [28]. At finite temperature, the displacement of an atom in AS deviate from the position in the LRC at zero temperature is a vector sum of the static displacement $u_s$ and thermal vibration displacement $u_T(t)$ from the zero temperature configuration of AS, $t$ is the time moment. In ordinary absorption experiment, time interval $T$ is much longer than the period of the slowest mode, therefore $\overline{E_U^C} = \frac{1}{T} \int_0^T dt \zeta^C (\frac{u_s + u_T(t)}{a})^2 |V_c|$. Atoms vibrate around their equilibrium points in AS, the time average of the cross term $u_s \cdot u_T(t)$ is zero. Thus Urbach energy from static disorder and from thermal disorder is additive [24] $\overline{E_U^C} = E_{U,s}^C + E_{U,T}^C$, $E_{U,s}^C = \zeta^C (\frac{u_s}{a})^2 |V_c|$. Thermal part $E_{U,T}^C = \zeta^C \frac{k_B T}{B_C} |V_c|$, $\overline{u_T^2} = \frac{1}{T} \int_0^T dt [u_T(t)]^2$ is the long time average of the square of amplitude of vibration. An ultra-fast probe of absorption edge may find oscillating in $\overline{E_U^C}$. Since $\overline{u_T^2} \propto \frac{k_B T}{B_C} a^2$ [12], $B_C$ is binding energy in the diluter regions where conduction tail states are localized, $E_{U,T}^C = \zeta^C k_B T \frac{|V_c|}{B_C}$. $\overline{E_U^C}$ linearly increases with temperature. Similarly result holds for $\overline{E_U^V}$. The is consistent with the fact that above 350K absorption edge linearly increase with $k_BT$ in a-Si:H [29, 30]. Because $B_V > B_C$, $E_U^C$ is more susceptible to thermal disorder than $E_U^V$ [31], as observed in ref. [30].

For realistic amorphous solid with topological disorder, by viewing an AS as many distorted regions relative to corresponding LRC, we push forward essential understanding on localized states confined in one distorted region. The predicted IPR, mobility edge, the dependence on static disorder and on temperature of the decay rate of band tails agree with available experiments and simulations. We explained the fact that valence tail states are more localized in a denser region with smaller BA and shorter BL and conduction tail states are more localized in diluter region with longer BL and larger BA in a-Si [7, 20]. Localized states in several distorted regions and other problems involving global topology will be addressed in future.

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