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Spectral limits for disordered semiconductors and their interfaces

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A spectral limit theorem is proved for semiconducting systems without crystal periodicity, generalizing earlier theorems involving model Hamiltonians for amorphous semiconductors and substitutional alloys. The theorem treats the combined effects of substitutional chemical disorder, bond-strength fluctuations, and noncrystalline topology. The allowed one-electron spectrum is shown to be contained in the union of the one-electron spectra associated with a collection of hypothetical bulk Hamiltonians corresponding to the various bond types in the system. Applications to simple models representative of the $Al_xGa_{1-x}As$-GaAs interface, the Si grain boundary, and amorphous Si and GaAs are discussed.

Theorems which place rigorous bounds on one-electron spectra of model tight-binding Hamiltonians have proved useful in understanding the properties of both chemically[1] and topologically[2–4] disordered systems. Such theorems have been of two types. The first type applies only to chemically disordered alloys with random single-site energies on an ordered lattice. The spectrum of the alloy is found to be a subset of the union of the spectra of the bulk constituents. The second type explores the effects of topological disorder and neglects chemical disorder. Within a restricted tight-binding model for a semiconductor, it is shown that the size of the band gap is independent of the connectivity of the lattice, provided that all interatomic bond strengths, intra-atomic couplings, and single-site energies have their bulk crystal values. Bounds can also be placed on the effects of bond-strength fluctuations.[3]

In this paper we prove a more general theorem which applies to systems containing both chemical and topological disorder. This theorem is proved for a model Hamiltonian for sp^3-bonded systems such as semiconductors, having the form

$$\mathscr{H}=\sum_{n,i}\epsilon^n\,|n,i\rangle\langle n,i| + \sum_{n,i,i'} V_1^n\,|n,i\rangle\langle n,i'| + \sum_{n,i} V_2^{n,n_i'}\,|n,i\rangle\langle n_i',i| \;. \tag{1}$$

Here the ket $|n,i\rangle$ denotes an sp^3 hybrid lobe at the atomic site n with its direction specified by the index i (cf. Fig. 1). In the last term n_i' denotes the nearest-neighbor atom to that at the site n in the direction defined by the lobe i. The atoms do not necessarily constitute a crystalline lattice; the connectivity of the lattice could, for example, correspond to five- and seven-membered rings, which are believed to be present in amorphous semiconductors.[5] The ϵ^n are single-site energies, while V_1^n couple different sp^3 lobes on the same atom and determine the s-p splitting in the solid. The variation of the ϵ^n and V_1^n from site to site corresponds to the inclusion of different types of atoms. Finally, $V_2^{nn_i'}$ is the nearest-neighbor bond strength, which is determined by the chemistry of the constituents and the interatomic distances. Recent extended x-ray-absorption fine-structure (EXAFS) studies[6] have shown that the latter can have a significant variation even in substitutional alloys.

Before stating and proving the theorem, we wish to observe that the spectral limits obtained using it will not, in general, agree quantitatively with those obtained in realistic calculations performed using techniques such as the self-consistent pseudopotential[7] and empirical tight-binding methods.[8] First, $\mathscr{H}$ is not accurate enough to provide a precise description of real systems. The restriction to nearest-neighbor hopping, for example, precludes the possibility of obtaining accurate semiconductor band structures for periodic systems and excludes the effects of dihedral angle fluctuations[8,9] in amorphous systems. Furthermore, in noncrystalline systems the bond angles are expected to vary about their crystalline values.[10] The variations should cause V_1^n in the second term of (1) to depend on i and i' in addition to n; this is not accounted for in the theorem. Second, as will be seen below, the theorem does not discriminate sensitively between varying atomic configurations. For example, the spectral limits it

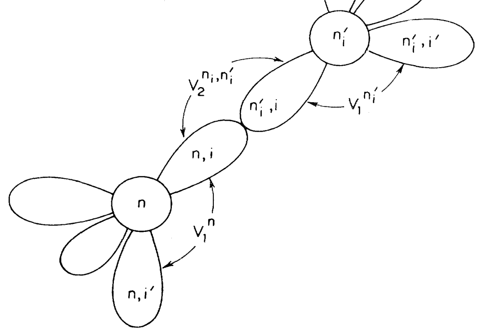

FIG. 1. Schematic illustration of model Hamiltonian [cf. Eq. (1)]. Atoms are denoted by n and sp^3 hybrid lobes by i. V_1 and V_2 are intra-atomic and interatomic couplings, respectively.

predicts for a single weakened bond are identical to those for a cluster of weakened bonds, while the two systems are physically expected to have quite different spectral limits. This drawback is also present in the earlier theorems.

The theorem states that

$$\text{Spec}\,\mathscr{H} \subset \bigcup_{(\mu)} \text{Spec}\,\mathscr{H}^{\mu}\ , \tag{2}$$

where

$$\text{Spec}\,\mathscr{H} = [E_v^{\text{bot}}(\mathscr{H}), E_v^{\text{top}}(\mathscr{H})] \cup [E_c^{\text{bot}}(\mathscr{H}), E_c^{\text{top}}(\mathscr{H})]\ ,$$

with similar definitions for Spec H^{μ}. Here $E_{v,c}^{\text{bot,top}}$ are the valence- and conduction-band lower and upper edges. The union in Eq. (2) is over all bond types present in $\mathscr{H}$; a bond type μ is defined by a pair of lobes $|m,j\rangle$ and $|m_j',j\rangle$ pointing at each other and the associated energy parameters ϵ^m, $\epsilon^{m_j'}$, V_1^m, $V_1^{m_j'}$, and $V_2^{mm_j'}$. Given a bond type μ we associate with it a bulk Hamiltonian H^{μ} obtained by replicating μ-type bonds to form a zinc-blende lattice, i.e.,

$$\begin{aligned} H^{\mu} = {} & \sum_{n\in S_1} \left[\epsilon^m \sum_i |n,i\rangle\langle n,i| + V_1^m \sum_{\substack{i\neq i \\ i,i'}} |n,i\rangle\langle n,i'| \right] \\ & + \sum_{n\in S_2} \left[\epsilon^{m_j'} \sum_i |n,i\rangle\langle n,i| + V_1^{m_j'} \sum_{\substack{i\neq i' \\ i,i'}} |n,i\rangle\langle n,i'| \right] \\ & + V_2^{m,m_j'} \sum_{n,i} |n,i\rangle\langle n_i',i|\ , \end{aligned} \tag{3}$$

where S_1 and S_2 represent the two fcc sublattices of a zinc-blende lattice.

Proving the theorem is equivalent to showing that

$$E_{c,v}^{\text{top}}(\mathscr{H}) \leq \max_{(\mu)} E_{c,v}^{\text{top}}(H^{\mu}) \tag{4}$$

and

$$E_{c,v}^{\text{bot}}(\mathscr{H}) \geq \min_{(\mu)} E_{c,v}^{\text{bot}}(H^{\mu})\ . \tag{4'}$$

To prove (4) we begin by defining two additional Hamiltonians associated with $\mathscr{H}$ and the H^{μ}, respectively,

$$\mathscr{H}_{\text{mol}} = \sum_{n,i} (\epsilon^n - V_1^n)\,|n,i\rangle\langle n,i| + \sum_{n,i} V_2^{n,n_i'}\ |n,i\rangle\langle n_i',i|$$

and

$$\begin{aligned} H_{\text{mol}}^{\mu} = {} & \sum_{n\in S_1} (\epsilon^m - V_1^m) \sum_i |n,i\rangle\langle n,i| \\ & + \sum_{n\in S_2} (\epsilon^{m_j'} - V_1^{m_j'}) \sum_i |n,i\rangle\langle n,i| \\ & + V_2^{m,m_j'} \sum_{n,i} |n,i\rangle\langle n_i',i|\ . \end{aligned}$$

Each of these Hamiltonians contains no intra-atomic couplings and therefore consists of isolated two-level molecules. The shift in the single-site energies in the H_{mol}^{μ} is included in order to ensure that

$$E_{c,v}^{\text{top}}(H_{\text{mol}}^{\mu}) = E_{c,v}^{\text{top}}(H^{\mu})\ , \tag{5}$$

which is easily verified by direct diagonalization of the secular determinants at Γ, where the band extrema lie.

Since each bond type in $\mathscr{H}$ corresponds to an H^{μ}, and therefore each molecule in $\mathscr{H}_{\text{mol}}$ corresponds to an H_{mol}^{μ}, we have

$$\text{Spec}\,\mathscr{H}_{\text{mol}} = \bigcup_{(\mu)} \text{Spec}\,H_{\text{mol}}^{\mu}$$

and

$$E_{c,v}^{\text{top}}(\mathscr{H}_{\text{mol}}) = \max_{(\mu)} E_{c,v}^{\text{top}}(H_{\text{mol}}^{\mu})\ . \tag{6}$$

Therefore, with the use of (5), (4) will be proved if we can demonstrate that

$$E_{c,v}^{\text{top}}(\mathscr{H}) \leq E_{c,v}^{\text{top}}(\mathscr{H}_{\text{mol}})\ . \tag{7}$$

To prove (7), we define

$$\mathscr{H}(\lambda) = \mathscr{H}_{\text{mol}} + \lambda \mathscr{H}_1\ , \tag{8}$$

where

$$\mathscr{H}_1 = \sum_{n,i,i'} V_1^n\,|n,i\rangle\langle n,i'|\ . \tag{9}$$

For $\lambda=0$, $\mathscr{H}(\lambda)$ is equal to $\mathscr{H}_{\text{mol}}$ and has isolated molecular levels, while for $\lambda=1$, $\mathscr{H}(\lambda)$ is equal to $\mathscr{H}$ and has fully developed valence and conduction bands; the $i=i'$ terms in (9) cancel the single-site energy shifts in $\mathscr{H}_{\text{mol}}$. Let $\psi_l(\lambda)$ be an eigenstate of $\mathscr{H}(\lambda)$ with energy $E_l(\lambda)$ in either the valence or conduction band. Then by first-order perturbation theory

$$\frac{dE_l(\lambda)}{d\lambda} = \langle \psi_l(\lambda)\,|\,\mathscr{H}_1\,|\,\psi_l(\lambda)\rangle\ . \tag{10}$$

Now , $\mathscr{H}_1$ is a decoupled collection of 4×4 matrices, each having the form

$$V_1^n \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}\ .$$

This matrix has three eigenvalues at zero and one at $4V_1^n \leq 0$, and therefore by a well-known theorem of linear algebra,

$$\langle \psi_l(\lambda)\,|\,\mathscr{H}_1\,|\,\psi_l(\lambda)\rangle \leq 0\ .$$

Using (10), we then have

$$E_l(1) - E_l(0) = \int_0^1 d\lambda \frac{dE_l(\lambda)}{d\lambda} \leq 0\ ,$$

so that

$$E_l(1) \leq E_l(0) \quad \text{for each } l\ .$$

Since $E_l(0)$ is an eigenvalue of $\mathscr{H}_{\text{mol}}$, it follows that

$$E_l(1) \leq E_{\text{c,v}}^{\text{top}}(\mathscr{H}_{\text{mol}})$$

according to whether l is in the valence band or the conduction band. Then (7), and therefore (4), are proved.

The technique used to prove (4′) is essentially parallel to the above and will not be described further.

We now describe some applications of the theorem to physical systems. Despite the simplicity of the model used the theorem contains enough physical ingredients to elucidate the most important factors which determine the band gap of a disordered system. For example, the relation of the gap of $\mathscr{H}$ to the local bond characteristics embodied in the $\mathscr{H}^{\mu}$ emphasizes the importance of short-range order versus long-range order in determining the band gap.[11] Furthermore, although the theorem as stated says nothing about the magnitude of the density of states in various energy ranges, one may be able to obtain a qualitative description of the electronic structure associated with $\mathscr{H}$ by assigning weights to the corresponding H^{μ} in accordance with physical intuition. Thereby one can discriminate between gaps, pseudogaps, and nongaps. Thus the theorem can provide physical insight without elaborate calculations provided accurate calculations or experiments on closely related systems exist.

(a) $Al_xGa_{1-x}As$ — GaAs interface. We will assume that no Al—Al, Ga—Ga, As—As, or Al—Ga bonds are formed, which would appear to be a reasonable assumption in view of the large energy penalty involved in forming such bonds. We will also assume that no bonds are weakened. Then the theorem states that whether or not the interface is abrupt, and independent of the orientation of the interface, the spectrum of $\mathscr{H}$ is contained in the union of the spectra of a GaAs bulk Hamiltonian and an AlAs bulk Hamiltonian. Since the AlAs band gap contains that of the GaAs,[12] it follows that there are no states inside the GaAs gap. This conclusion is compatible with realistic band-structure results[13] for abrupt AlAs-GaAs interfaces, which showed no states inside the GaAs gap, and with experiments on broadened (~ 100 Å) $Al_xGa_{1-x}As$-GaAs interfaces,[14] which showed a very low density (less than 5×10^{10} cm^{-2}) of gap states, presumably associated with defects.

(b) Si grain boundary. We make no specific assumptions regarding the interface geometry, but take the ϵ^n and the V_1^n to be constant and allow the bond strengths V_2 to vary. Then the H^{μ} which determine the spectrum of $\mathscr{H}$ are all identical to a bulk Si Hamiltonian, except that they have different values of V_2. The H^{μ} with the smallest value of V_2 will then determine the limits of the allowed spectrum. If this value of V_2 is only slightly less than the bulk value, then the band gap of the associated H^{μ} will be slightly smaller than the bulk band gap and there will be no states at or near midgap. If, on the other hand, there are values of V_2 much smaller than the bulk value, then the allowed spectrum of $\mathscr{H}$ will include the entire band gap. These results provide a framework for interpreting experimental data on interface states at Si grain boundaries. With the use of I-V characteristics an interface state density of roughly 10^{12} cm^{-2}, or roughly one for every thousand interface atoms, at energies within a few tenths of an eV of midgap, has been measured.[15] The spectral-limit-theorem results would suggest, in agreement with the usual interpretation, that these levels are due to a small density of severely weakened or broken bonds; even a large density of slightly weakened bonds would only be expected to produce tails near the band edges.

This case illustrates the above-mentioned inability of the theorem to sensitively discriminate between varying atomic configurations. For severely weakened bonds the theorem allows the whole gap to be filled in nearly uniformly, which would be correct if the weakened bonds formed large clusters. In contrast, the physical system has a density of states strongly peaked near midgap, presumably corresponding to isolated weakened bonds.

(c) Amorphous Si and GaAs. In these systems we will assume that all of the ϵ^n, V_1^n, and $V_2^{nn'_i}$ are equal to their bulk-crystal values and focus on the possible effects of the changes in connectivity associated with the amorphous structure. For Si, all of the H^{μ} are then equivalent to a bulk Si Hamiltonian, even if the structure contains five- and seven-membered rings. The band gap of the amorphous structure is then at least as large as that of the bulk crystal, in agreement with earlier theorems.[2-4] The same analysis holds for GaAs, provided that no Ga—Ga or As—As bonds are present (then there are of course no five- or seven-membered rings); as mentioned earlier, the density of such bonds is expected to be small from energetic considerations. If one takes the possibility of such bonds into account, then the H^{μ} corresponding to Ga—Ga or As—As bonds have spectra which fill in the GaAs band gap, consistent with the intuitive expectation that such bonds should cause gap states.[16]

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