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INTERNATIONAL CENTRE FOR
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BONDED AMORPHOUS SOLIDS

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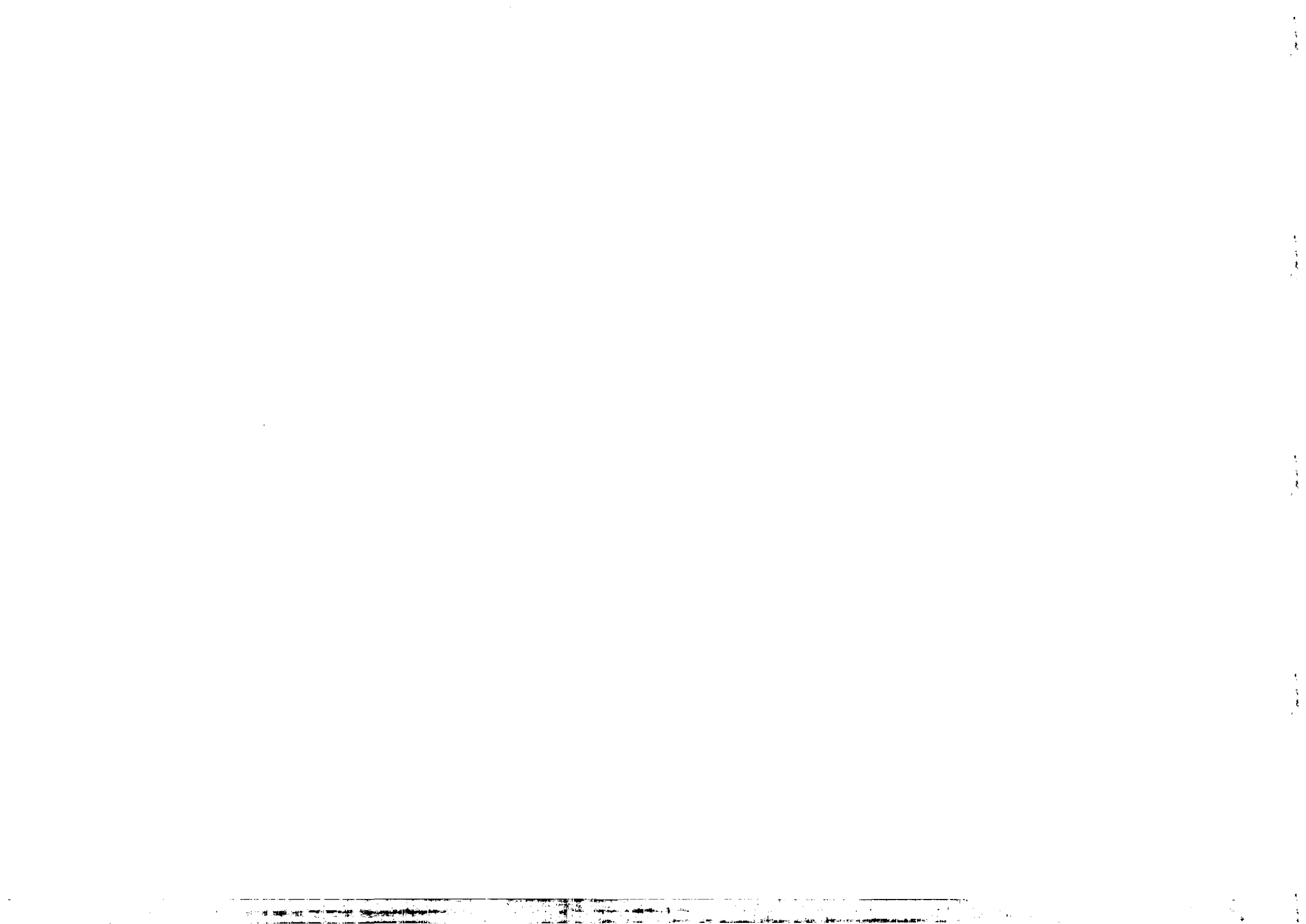**INTERNATIONAL
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A CALCULATION OF THE ENERGY GAP IN TETRAHEDRALLY

BONDED AMORPHOUS SOLIDS*

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ABSTRACT

By using quantum mechanics calculation, we present a straightforward
method to give the bounds for the electronic density of state in tetrahedrally
bonded amorphous solids. The results are quite consistent with Weaire's which
are obtained using the diagram method.

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Weaire and others have proposed a tight-binding Hamiltonian for the
topologically disordered structure. By using the diagram method he proved that
there would be an energy gap in such amorphous solids[1-3]. The purpose of this
paper is to present another straightforward calculation to give the bounds for
the electronic density of states by calculating the expectation value of the
energy from tight-binding Hamiltonian.

In Dirac notation, we can write the model Hamiltonian as follows:

$$\hat{H} = \sum_{i;\, j \neq j'} V_1 |i,j\rangle\langle i,j'| + \sum_{j;\, i \neq i'} V_2 |i,j\rangle\langle i',j| \tag{1}$$

where the indices i and i' refer to the atoms, j and j' to the bonds; ket
vector $|i,j\rangle$ ($j =/\sim 4$) represent the four hybridized SP^3 orbitals associated
with the atom i. These localized basis functions $|i,j\rangle$ form an orthonormal
set, that means $\langle i,j |i',j'\rangle = \delta_{ii'}\, \delta_{jj'}$. The matrix element $V_1 = \langle i,j | H|i,j'\rangle$
is the interaction between different orbitals j and j' at the same site atom i,
and $V_2 = \langle i,j |H| i',j\rangle$ describes the interaction between partner orbitals
of the nearest neighbour atoms i and i' (cf. Fig. 1). V_1 and V_2 are taken as
constants for all the atoms of the disordered network.

Consider a single isolated atom, for which the Hamiltonian (1) reduces
to
$$\hat{H}_{atom} = \sum_{j \neq j'} V_1 |j\rangle\langle j'|$$

Similarly, for an isolated "bond pair"
$$\hat{H}_{bond\ pair} = V_2 |i,j\rangle\langle i',j|$$

Substituting the wave function $|\psi\rangle = \sum_{s,t} C_{st} | s,t\rangle$ into the Schrödinger
equations $H_a |\psi\rangle = \varepsilon_a |\psi\rangle$ and $H_{b.p} |\psi\rangle = \varepsilon_{b.p} |\psi\rangle$, we can separately obtain
the following energy eigenvalues:

$$\mathcal{E}_a = 3V_1,\ -V_1,\ -V_1,\ -V_1$$
and
$$\mathcal{E}_{b.p} = V_2,\ -V_2$$

For the former, these levels correspond to an S -orbital and triply degenerated P-orbitals, that means we should take $V_1 < 0$; for the latter, these levels correspond to bonding orbital $\sqrt{2}(\,|\,i,j>+\,|\,i',j>\,)$ and anti-bonding orbital $\sqrt{2}(\,|\,i,j>-\,|\,i',j>\,)$. Hence V_2 should also be taken negative to give the bonding orbital lower energy.

In the tight-binding LCAO approximation, the state wave functions $|\psi>$ are linear combinations of the above hybridized atom orbitals $\{|\,s,t>\}$:

$$|\psi> = \sum_{s,t} c_{st} \,|\,s,t> \tag{2}$$

where, we label the atoms by a site index s and the bonds by a site index t.

Substituting equations (1) and (2) into the Schrödinger equation

$$\hat{H}\,|\psi> = E\,|\psi> \quad ,$$

We can obtain the following result

$$M\,\vec{U}(i) = -V_2\,\vec{V}(i) \tag{3}$$

where, the matrix

$$M = \begin{bmatrix} -E & V_1 & V_1 & V_1 \\ V_1 & -E & V_1 & V_1 \\ V_1 & V_1 & -E & V_1 \\ V_1 & V_1 & V_1 & -E \end{bmatrix}$$

and has eigenvalues

$$\lambda_1 = -E + 3V_1$$
$$\lambda_2 = -E - V_1 \qquad \text{(triply degenerate)}$$

corresponding eigenvectors being $\vec{u}^s$ and $\vec{u}^p$.

$\vec{U}(i)$ and $\vec{V}(i)$ are four-dimensional vectors, their components are

$\vec{U}(i)$ – the four combinations c_{ij} (j= 1~4) of SP^3 orbitals associated with the site atom i

$\vec{V}(i)$ – the combination coefficient c_{ij} of the partner orbitals of four

nearest neighbour atoms associated with these bonds (cf. Fig.2).

The relation (3) holds at every site atom i of the disordered network.

We first proved the following equation:

$$\sum_{i} \vec{U}^* \cdot \vec{V} = \frac{E^2 - 2EV_1 - 3V_1^2 + V_2^2}{2 V_2 (E - V_1)} \tag{4}$$

Taking scalar product of both sides of equation (3) with the conjugate vector $\vec{U}^*$ of $\vec{U}$, we have

$$\vec{U}^* \cdot M\vec{U} = -V_2\,\vec{U}^* \cdot \vec{V} \tag{5}$$

By expanding $\vec{U}$ in eigenvectors of M

$$\vec{U} = c^s \vec{u}^s + c^p \vec{u}^p$$

substituting this expression into the left-hand side of (5), and summing up for all sites i, we get

$$\lambda_1 \sum_{i} |c^s|^2 + \lambda_2 \sum_{i} |c^p|^2 = -V_2 \sum_{i} \vec{U}^* \cdot \vec{V} \tag{6}$$

Weaire et al., have shown[2] :

$$\sum_{i} |c^s|^2 \Big/ \sum_{i} |c^p|^2 = \frac{V_2^2 - \lambda_2^2}{\lambda_1^2 - V_2^2} \quad ;$$

using

$$\sum_{i} |c^s|^2 + \sum_{i} |c^p|^2 = 1 \quad ,$$

we have

$$\sum_{i} |c^s|^2 = (V_2^2 - \lambda_2^2)/(\lambda_1^2 - \lambda_2^2)$$

and

$$\sum_{i} |c^p|^2 = (\lambda_1^2 - V_2^2)/(\lambda_1^2 - \lambda_2^2) \quad .$$

Thus the following result can be obtained from equation (6):

$$\sum_{i} \vec{U}^* \cdot \vec{V} = -V_2^{-1} \left[\frac{\lambda_1 V_2^2 - \lambda_1 \lambda_2^2 + \lambda_2 \lambda_1^2 - \lambda_2 V_2^2}{\lambda_1^2 - \lambda_2^2} \right]$$

$$= -V_2^{-1} \left[\frac{(\lambda_1 - \lambda_2) V_2^2 + (\lambda_1 - \lambda_2) \lambda_1 \lambda_2}{\lambda_1^2 - \lambda_2^2} \right]$$

$$= -V_2^{-1} \cdot \frac{(\lambda_1 - \lambda_2)(V_2^2 + \lambda_1 \lambda_2)}{(\lambda_1 - \lambda_2)(\lambda_1 + \lambda_2)}$$

$$= -\frac{V_2^2 + \lambda_1 \lambda_2}{V_2(\lambda_1 + \lambda_2)}$$

$$= -\frac{V_2^2 + (E^2 - 2EV_1 - 3V_1^2)}{V_2(-2E + 2V_1)}$$

$$= \frac{E^2 - 2EV_1 - 3V_1^2 + V_2^2}{2V_2(E - V_1)}$$

This is just the equation (4).

Now we can further calculate the expectation value of the energy

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

By using the normalization condition for the wave function,

$$\langle \psi | \psi \rangle = \sum_{i,j} \sum_{i',j'} c_{ij}^* c_{i'j'} \langle i,j | i',j' \rangle$$

$$= \sum_{i,j} \sum_{i',j'} c_{ij}^* c_{i'j'} \delta_{ii'} \delta_{jj'} = \sum_{i,j} |c_{ij}|^2 = 1 \tag{7}$$

we obtain

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle \psi | H | \psi \rangle =$$

$$= \sum_{s,t} \sum_{s',t'} c_{st}^* c_{s't'} \langle s,t | \Big(V_1 \sum_{i; j \neq j'} |i,j\rangle\langle i,j'| +$$

$$+ V_2 \sum_{j; i \neq i'} |i,j\rangle\langle i',j| \Big) | s',t' \rangle$$

$$= \sum_{s,t} \sum_{s',t'} c_{st}^* c_{s't'} \Big\{ V_1 \sum_{i; j \neq j'} \langle s,t | i,j\rangle\langle i,j' | s',t'\rangle$$

$$+ V_2 \sum_{j; i \neq i'} \langle s,t | i,j\rangle\langle i',j | s',t'\rangle \Big\}$$

$$= V_1 \sum_{\substack{s,t \\ s',t'}} \sum_{j \neq j'} c_{st}^* c_{s't'} \delta_{si} \delta_{tj} \delta_{is'} \delta_{j't'} +$$

$$+ V_2 \sum_{\substack{s,t \\ s',t'}} \sum_{i \neq i'} c_{st}^* c_{s't'} \delta_{si} \delta_{tj} \delta_{i's'} \delta_{jt'}$$

$$= V_1 \sum_{t \neq t'} \sum_{s,s'} c_{st}^* c_{s't'} \delta_{ss'} + V_2 \sum_{s \neq s'} \sum_{t,t'} c_{st}^* c_{s't'} \delta_{tt'}$$

$$= V_1 \sum_{s; t \neq t'} c_{st}^* c_{st'} + V_2 \sum_{t; s \neq s'} c_{st}^* c_{s't} \tag{8}$$

Considering $\sum_{s \neq s'} \sum_{t} c_{st}^* c_{s't} = \sum_i \vec{U}^* \cdot \vec{V}$ and noting equation (4), we can obtain from equation (8):

$$E = V_1 \sum_{s; t \neq t'} c_{st}^* c_{st'} + \frac{1}{2} \cdot \frac{E^2 - 2EV_1 - 3V_1^2 + V_2^2}{E - V_1}$$

$$= V_1 A + \frac{1}{2} \cdot \frac{E^2 - 2EV_1 - 3V_1^2 + V_2^2}{E - V_1} \qquad ,$$

where we have set

$$A = \sum_s \sum_{t \neq t'} c_{st}^* c_{st'} \qquad .$$

After arranging the above equation in order, we have a simple algebraic equation

$$E^2 - 2V_1 A E + (2V_1^2 A + 3V_1^2 - V_2^2) = 0 \qquad .$$

its two roots are

$$E_{1,2} = V_1 A \mp \sqrt{V_1^2 A^2 - 2V_1^2 A - 3V_1^2 + V_2^2} \tag{9}$$

Then again, from the algebraic identities we can write out

$$A = \sum_s \sum_{t \neq t'} c_{st}^* c_{st'} = \sum_s \Big\{ |\sum_t c_{st}|^2 - \sum_t |c_{st}|^2 \Big\}$$

$$= \sum_s \Big\{ 3 \sum_t |c_{st}|^2 - \sum_{t > t'} |c_{st} - c_{st'}|^2 \Big\}$$

Using the result in equation (7), the following relations can be obtained:

$$(A)_{min} = -\sum_{s,t} |c_{st}|^2 = -1$$

(when each $\sum_t C_{st} = 0$)

$$(A)_{max} = 3 \sum_{s,t} |C_{st}|^2 = 3$$

(when every $C_{st} = C_{st'}$)

so that,

$$E_1 = V_1 A - \sqrt{V_1^2 A^2 - 2 V_1^2 A - 3 V_1^2 + V_2^2}$$

$$(E_1)_{min} = 3V_1 + V_2$$

$$(E_1)_{max} = -V_1 + V_2 \qquad (\because \sqrt{V_2^2} = -V_2)$$

similarly,

$$E_2 = V_1 A + \sqrt{V_1^2 A^2 - 2 V_1^2 A - 3 V_1^2 + V_2^2}$$

$$(E_2)_{min} = 3V_1 - V_2$$

$$(E_2)_{max} = -V_1 - V_2 .$$

Comparing E_1 with E_2 , we can easily see that E_1 belongs to the valence band, E_2 to the conduction band.

Thus we can determine the bounds on the energy band as follows:

valence band ΔE_1

$$3V_1 + V_2 \quad \sim \quad - V_1 + V_2$$

conduction band ΔE_2

$$3V_1 - V_2 \quad \sim \quad - V_1 - V_2$$

width of the energy band

$$\Delta d_v = \Delta d_c = -4 V_1$$

energy gap

$$\Delta g = (3V_1 - V_2) - (-V_1 + V_2) = 4V_1 - 2V_2$$

The condition under which the energy gap can exist is $\Delta g > 0$ or $\dfrac{V_1}{V_2} < \frac{1}{2}$. For the case of $V_1/V_2 \geqslant \frac{1}{2}$, we have $\Delta g \leqslant 0$, and that means the bands overlap with the energy gap disappearing naturally.

From the above discussions we can draw the conclusion:

For tetrahedrally bonded amorphous solids, only under the condition $V_1/V_2 < \frac{1}{2}$ the energy gap can exist, its value is $4V_1 - 2V_2 > 0$.

The allowed electronic density regions are shown in Fig. 3 for such amorphous semiconductor.

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[2] D. Weaire and M.F. Thorpe, Phys. Rev. B4, 2508 and 3518 (1971).

[3] B. Kramer and D. Weaire, "Theory of electronic states in amorphous semi-conductors" in "Topics in applied physics - amorphous semiconductors", vol. 36, 9 (1979).

FIGURE CAPTIONS

Fig. 1. Basis functions and interactions in the Weaire Hamiltonian.

Fig. 2. Directed orbitals in the Weaire model. The coefficients C_{ij} of basis functions 1~4 form the vector $\vec{U}$, those of (1'~4') form $\vec{V}$.

Fig. 3. The electronic density regions in tetrahedrally bonded amorphous solids.

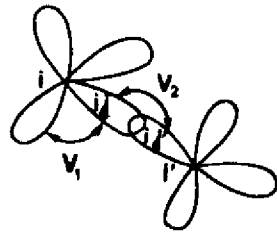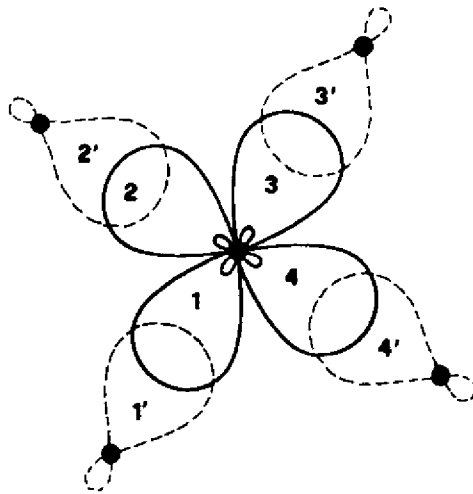Fig.1

Fig.2

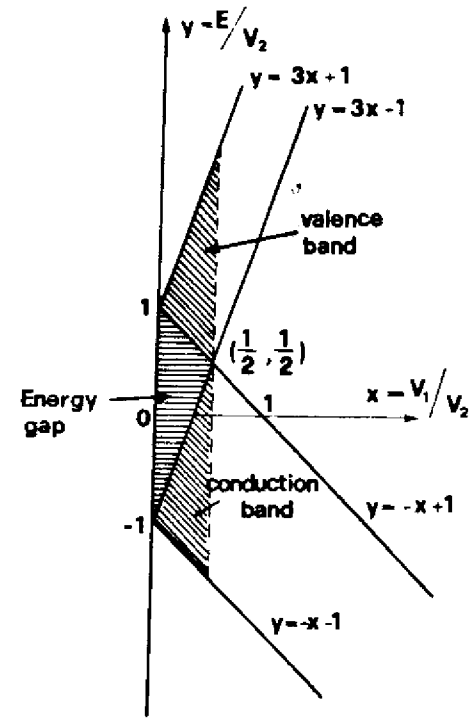

Fig.3

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