

## Molecular-Orbital Studies of the Electronic States of Amorphous Selenium

Inan Chen

Xerox Rochester Research Center, Rochester, New York 14644

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The electronic energy structure of Se chains and rings are studied by a molecular-orbital approach, i. e., using the hybrid orbitals as bases and using the semiempirical Hamiltonian matrix elements. The choices of the bases and the semiempirical parameters are discussed. The calculated density of states is in excellent agreement with that obtained for amorphous Se by photoemission experiments (Nielsen). The simulated joint density of states resembles the observed  $\epsilon_2$  spectra (Leiga, Stuke). A new interpretation for the double peaks in the valence-band density of states and in the  $\epsilon_2$  spectra is given.

### I. INTRODUCTION

Solid selenium exists in three different modifications: trigonal and monoclinic crystalline, and amorphous (or vitreous) forms. The trigonal crystals<sup>1</sup> consist of threefold helical chains (Fig. 1) while the monoclinic crystals<sup>2</sup> are built of eight-membered puckered rings (Fig. 2). It is believed that in the amorphous form both chains and rings coexist.<sup>3</sup> The chains or rings are held together in the solid by van der Waals-type forces which are much weaker than the covalent bonds between atoms of the same chain or ring. This makes selenium one of the few inorganic molecular solids.

Only two of the six valence electrons in a Se atom participate in the bonding within a chain (or ring). The other four electrons form two sets of lone pairs. The coordination of the atoms does not belong to the cubic or tetrahedral symmetry so that the atomic  $p$  orbitals or the tetrahedral (equivalent)  $sp^3$  hybrids are not good representations. These features, together with the above-mentioned molecular nature of the solids, distinguish Se from other well-studied semiconductors, such as group-IV elemental semiconductors or the II-VI and III-V compounds.

Theoretical studies of the electronic structures of solid Se have been reported by many authors. The most recent and complete ones are the pseudopotential calculations by Sandrock,<sup>4</sup> and by Kramer and co-workers.<sup>5</sup> The former treated the band structure of trigonal Se, while the latter dealt with the amorphous form by imposing a configurational average to the results obtained by Sandrock.<sup>4</sup> In both cases the calculated  $\epsilon_2$ , the imaginary part of the dielectric function, is in excellent agreement with the experimental ones.<sup>6,7</sup> However, the energies of the valence bands (especially the deeper ones) are quite doubtful.<sup>8</sup> Nielsen's photoemission experiment<sup>8</sup> with 21.2-eV photons indicates that the entire valence band of amorphous Se extends not more than 9 eV from the top edge. Kramer's calculation<sup>5</sup> for amorphous Se gives the width of the

upper two (triplet) valence bands as  $\sim 8$  eV. The lowest triplet band (not included in Kramer's calculation<sup>5</sup>), which should not be distorted very much from the trigonal crystal values, extends more than 15 eV below the top edge, according to Sandrock.<sup>4</sup> These deep-lying states have not been detected in Nielsen's careful search.<sup>8</sup> (See Fig. 1 of Ref. 8.)

In the calculations of Sandrock<sup>4</sup> and Kramer *et al.*<sup>5</sup> the distinct features of solid Se mentioned above have not been taken into account explicitly. Tutihasi and Chen<sup>6</sup> have attempted to incorporate these special features by adopting the hybrid orbitals of  $s$  and  $p$  atomic orbitals, constructed according to the crystal symmetry, as the bases for the band-structure calculation of trigonal Se. Although no quantitative calculation of the band structure has been carried out, it has been possible to assign all peaks in the  $\epsilon_2$  spectra based on symmetry arguments. As pointed out by Nielsen, this molecular-orbital approach gives a better agreement with experiment in the width of total valence band.

Molecular-orbital methods have been used to interpret the carrier-transport properties in orthorhombic sulfur by Spear and co-workers<sup>9</sup> and by Chen.<sup>10</sup> Kastner<sup>11</sup> has recently discussed the electronic structures of chalcogenide semiconductors in terms of bonding bands and lone-pair bands. Messmer and Watkins<sup>12</sup> have studied the energies of the defect states in the tetrahedrally bonded (covalent) semiconductors by molecular-orbital calculations. In this symmetry the  $s$  and the three  $p$  orbitals, respectively, belong to an irreducible representation.

In this paper we extend the molecular-orbital calculation of Ref. 6 to the description of the electronic states of amorphous Se. The interaction between the neighboring bonds and lone pairs are considered. The effect of disorder is treated by imposing a Gaussian distribution on each energy level calculated assuming the short-range order. Both chain and ring states are considered. The

results are in excellent agreement with the photoemission<sup>8</sup> and the optical reflectance<sup>7</sup> measurements. The molecular-orbital (MO) method used to calculate the energy levels is discussed in Sec. II, and the calculations for chains and rings are described in Secs. III and IV, respectively. In Sec. V we compare the results of calculation with the experimentally observed density of states and the  $\epsilon_2$  spectra.

## II. SEMIEMPIRICAL MO CALCULATIONS

The MO calculations are carried out in the framework of the Wolfsberg-Helmholz semiempirical method.<sup>13</sup> In this method, the matrix elements of the Hamiltonian are approximated by

$$H_{kk} = E_k, \quad (2.1)$$

$$H_{kl} = F_{kl} S_{kl} (E_k + E_l) / 2, \quad k \neq l, \quad (2.2)$$

where  $E_k$  is the valence-state energy of the orbital  $k$ ,  $S_{kl}$  is the overlap integral between the orbitals  $k$  and  $l$ , and  $F_{kl}$  is a parameter which may or may not depend on  $k$  and  $l$ . The physical basis of the approximation, Eq. (2.2), has been discussed by several authors.<sup>14</sup>

Since, as shown in the following, the approximation, Eq. (2.2), is not invariant with respect to a

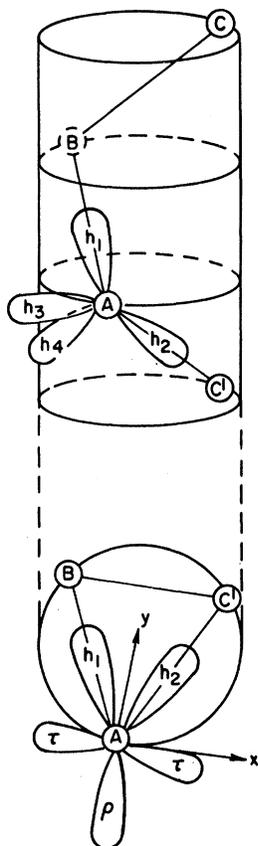


FIG. 1. Hybrid orbitals of Se in a helical chain.

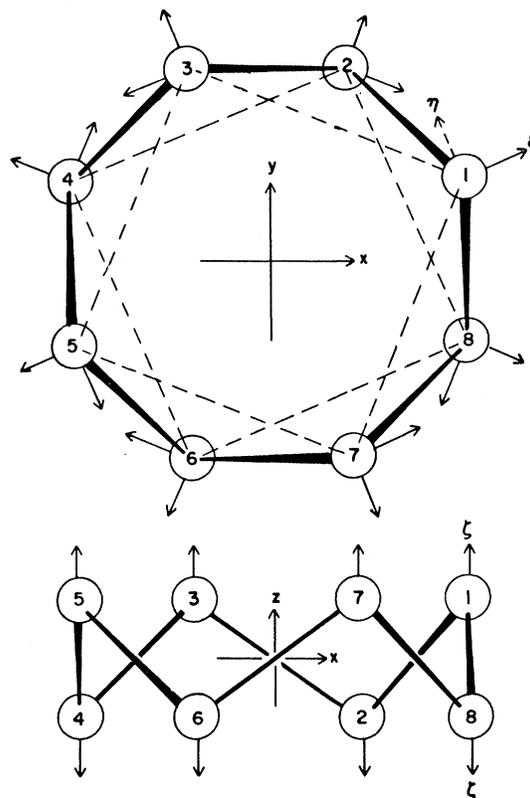


FIG. 2. Structure of the Se ring molecule. Top: viewed perpendicular to the molecular planes. Bottom: viewed parallel to the molecular planes.

unitary transformation of the basis orbitals (e.g., hybridization), it is important to choose an appropriate set of bases. A hybrid orbital  $h_{ik}$ , on atom  $i$ , is represented by a linear combination of atomic orbitals  $a_{im}$  as

$$h_{ik} = \sum_m B_{ikm} a_{im}. \quad (2.3)$$

The Hamiltonian matrix elements with  $h_{ik}$  as bases are related to those with  $a_{im}$  as bases by

$$H_{ik,jl} = \sum_m \sum_n B_{ikm} B_{jln} H_{im,jn}, \quad (2.4)$$

where  $i$  and  $j$  refer to the atoms,  $k$  and  $l$  to the hybrids, and  $m$  and  $n$  to the atomic orbitals.

*Case I:* diagonal elements,  $i=j$  and  $k=l$ . Using the approximation, Eq. (2.2), in the right-hand side of Eq. (2.4) we have

$$\begin{aligned} H_{ik,ik} &= \sum_m B_{ikm} B_{ikm} H_{im,im} \\ &+ \frac{1}{2} \sum_m \sum_{n \neq m} B_{ikm} B_{ikn} F_{im, in} S_{im, in} (E_{im} + E_{in}) \\ &= \sum_m B_{ikm}^2 E_{im}. \end{aligned} \quad (2.5)$$

The second sum vanishes because of the orthogo-

nality of the atomic orbitals on the same atom ( $S_{lm,ln} = 0$ ,  $m \neq n$ ). Thus, the diagonal elements with hybrid bases can be expressed using only the diagonal elements with atomic-orbital bases.

*Case II:* elements between different hybrids of the same atom,  $i = j$  but  $k \neq l$ . Direct application of Eq. (2.2) yields

$$H_{ik,il} = \frac{1}{2} F_{ik,il} S_{ik,il} (H_{ik,ik} + H_{il,il}) = 0, \quad (2.6)$$

which results from the orthogonality of two hybrids on the same atom ( $S_{ik,il} = 0$ ,  $k \neq l$ ). However, if Eq. (2.2) is applied to the off-diagonal elements on the right-hand side of Eq. (2.4), with  $i = j$ , we have

$$\begin{aligned} H_{ik,il} &= \sum_m B_{ikm} B_{ilm} H_{im,im} \\ &+ \frac{1}{2} \sum_m \sum_{n \neq m} B_{ikm} B_{iln} F_{im,ln} S_{im,ln} (E_{im} + E_{ln}) \\ &= \sum_m B_{ikm} B_{ilm} E_{im}, \end{aligned} \quad (2.7)$$

which does not vanish in general.

*Case III:* elements between hybrids on different atoms,  $i \neq j$ . Applications of Eq. (2.2) on the right- and left-hand sides of Eq. (2.4) give Eqs. (2.8) and (2.9), respectively,

$$H_{ik,jl} = \frac{1}{2} \sum_m \sum_n B_{ikm} B_{jln} F_{im,jn} S_{im,jn} (E_{im} + E_{jn}), \quad (2.8)$$

$$\begin{aligned} H_{ik,jl} &= \frac{1}{2} F_{ik,jl} S_{ik,jl} (H_{ik,ik} + H_{jl,jl}) \\ &= \frac{1}{2} F_{ik,jl} \left( \sum_m B_{ikm}^2 E_{im} + \sum_n B_{jln}^2 E_{jn} \right) \\ &\quad \times \sum_m \sum_n B_{ikm} B_{jln} S_{im,jn}. \end{aligned} \quad (2.9)$$

The two expressions, Eqs. (2.8) and (2.9), are again not identical in general, even if the parameter  $F$  is a constant independent of the orbitals  $k, l, m, n$ .

Furthermore, if atomic orbitals are chosen as the bases, the requirement of invariance under coordinate rotation places some restriction on the explicit form of the parameter  $F$ .

Cusachs<sup>14(a)</sup> has suggested the formula

$$F_{kl} = 2 - |S_{kl}| \quad (2.10)$$

for the parameter. We shall show that this formula is not invariant under coordinate rotations.

Consider molecular orbitals constructed from atomic  $s$  and  $p$  orbitals. Under a coordinate rotation,  $s$  orbitals are invariant, and the  $p$  orbitals transform as

$$P_{il} = \sum_{m=x,y,z} R_{ilm} \hat{p}_{im}.$$

*Case IIA:*  $i = j$ ,  $k = s$ , and  $l \neq s$ . Equation (2.7) vanishes because  $B_{ism} = 0$  if  $m \neq s$ .

*Case IIB:*  $i = j$ ,  $k \neq s$ , and  $l \neq s$  ( $k \neq l$ ). Equation (2.7) reads

$$H_{ik,il} = \left( \sum_{m \neq s} R_{ikm} R_{ilm} \right) E_{ip} = 0, \quad (2.11)$$

owing to the orthogonality of the matrix  $R$ .

Thus the approximation Eq. (2.10) is invariant under rotation for off-diagonal elements belonging to the same atom.

*Case IIIA:*  $i \neq j$ ,  $k = s$ , and  $l \neq s$ . From Eqs. (2.8) and (2.9) we have Eqs. (2.12) and (2.13), respectively:

$$H_{is,jl} = \frac{1}{2} (E_{is} + E_{jp}) \sum_n R_{jln} F_{is,jn} S_{is,jn}, \quad (2.12)$$

$$H_{is,jl} = \frac{1}{2} (E_{is} + E_{jp}) F_{is,jl} \sum_n R_{jln} S_{is,jn}. \quad (2.13)$$

*Case IIIB:*  $i \neq j$ ,  $k \neq s$ , and  $l \neq s$ . In this case, Eqs. (2.8) and (2.9) read, respectively,

$$H_{ik,jl} = E_p \sum_m \sum_n R_{ikm} R_{jln} F_{im,jn} S_{im,jn}, \quad (2.14)$$

$$H_{ik,jl} = E_p R_{ik,jl} \sum_m \sum_n R_{ikm} R_{jln} S_{im,jn}. \quad (2.15)$$

It can be seen that the pairs of expressions, Eqs. (2.12) and (2.13) and Eq. (2.14) and (2.15), respectively, are not identical if the parameters  $F$  are given by Eq. (2.10).

The invariance of Eq. (2.2) under coordinate rotations can be obtained if a constant value is assigned to the parameter  $F_{isjp}$ , between an  $s$  orbital and all  $p$  orbitals, and another constant value to  $F_{ipjp}$ , between any two  $p$  orbitals, as well as a value for  $F_{isjs}$  between two  $s$  orbitals, for each pair of atoms  $i$  and  $j$ . These constant values of parameters may be determined by Eq. (2.10) with a suitable average value for  $|S_{kl}|$ .

As a simplest approach to take into account the anisotropic bonding feature of Se, we follow the idea of Ref. 6 and use the hybrid orbitals as the bases. In Sec. III we shall show the different results obtained with different sets of bases. As for the parameter  $F$ , Cusachs's formula,<sup>13</sup> Eq. (2.10), may be used for hybrid bases, but we shall also consider results obtained with various parameter values.

### III. CALCULATION OF CHAIN STATES

As developed in the previous papers,<sup>6</sup> the  $4s$  and  $4p$  atomic orbitals of Se atoms in a helical chain are hybridized into (i) two equivalent  $\sigma$  hybrids pointing toward the nearest neighbors,  $h_1$  and  $h_2$ , and (ii) two equivalent lone-pair hybrids,  $h_3$  and  $h_4$ . They can be written as

$$h_i = \gamma s + (1 - \gamma^2)^{1/2} p_i, \quad i = 1, 2 \quad (3.1)$$

$$h_j = (0.5 - \gamma^2)^{1/2} s + (0.5 + \gamma^2)^{1/2} p_j, \quad j = 3, 4$$

where the coefficient  $\gamma$  of the  $s$  orbital in  $h_i$  can be determined from the bond angle  $\theta$  ( $= 103.1^\circ$ )<sup>1</sup> as

$$\gamma = [-\cos\theta / (1 - \cos\theta)]^{1/2} = 0.430, \quad (3.2)$$

and  $p_i$ ,  $p_j$  are appropriate combinations of atomic  $p_x$ ,  $p_y$ , and  $p_z$  orbitals. Assuming the atomic positions in the trigonal Se structure, these combinations are given by

$$h_{1,2} = 0.430s \pm 0.324x + 0.562y \pm 0.628z, \quad (3.3)$$

$$h_{3,4} = 0.562s \pm 0.628x - 0.430y \pm 0.324z, \quad (3.4)$$

where the  $x$ ,  $y$ , and  $z$  axes are shown in Fig. 1.

The  $\sigma$  hybrids of two neighboring atoms  $A$  and  $B$ , pointing toward each other, interact strongly to form a bonding ( $\beta$ ) and an antibonding ( $\alpha$ ) orbital:

$$\beta = [h_{1A} + h_{2B}] / [2(1 + S_\sigma)]^{1/2}, \quad (3.5)$$

$$\alpha = [h_{1A} - h_{2B}] / [2(1 - S_\sigma)]^{1/2}, \quad (3.6)$$

where  $S_\sigma = \langle h_{1A} | h_{2B} \rangle$  is the overlap integral between the two  $\sigma$  hybrids.

In the discussion of the electronic states in trigonal Se,<sup>6</sup> we have considered the combinations of the two equivalent lone pairs such that each would transform according to one of the irreducible representations of the symmetry group ( $D_3$ ),

$$\rho = (h_3 + h_4) / \sqrt{2}, \quad (3.7)$$

$$\tau = (h_3 - h_4) / \sqrt{2}. \quad (3.8)$$

However, in the case of amorphous Se, this restriction may be relaxed.

The  $s$  and  $p$  characters of the  $\alpha$  and  $\beta$  orbitals are that of  $h_1$  and  $h_2$ , and are given in Eq. (3.3). The  $\tau$  orbital is of pure  $p$  character and the  $\rho$  orbital has twice the  $s$  character of the lone pair  $h_3$ , Eq. (3.4).

The energies of these basis orbitals are given in terms of  $E_s$  ( $-20.828$  eV)<sup>15</sup> and  $E_p$  ( $-10.786$  eV),<sup>15</sup> the valence-state energies of Se  $4s$  and  $4p$  atomic orbitals, as

$$E_1 = E_2 = \gamma^2 E_s + (1 - \gamma^2) E_p = -12.639 \text{ eV}, \quad (3.9)$$

$$E_3 = E_4 = (0.5 - \gamma^2) E_s + (0.5 + \gamma^2) E_p = -13.954 \text{ eV}, \quad (3.10)$$

$$E_\rho = (1 - 2\gamma^2) E_s + 2\gamma^2 E_p = -17.122 \text{ eV}, \quad (3.11)$$

$$E_\tau = E_p = -10.786 \text{ eV}, \quad (3.12)$$

$$E_\beta = (E_1 + E_{12}) / (1 + S_\sigma), \quad (3.13)$$

$$E_\alpha = (E_1 - E_{12}) / (1 - S_\sigma), \quad (3.14)$$

where  $E_{12}$  is the interaction energy between  $h_1$  and  $h_2$  of the neighboring atoms and can be evaluated simply by the semiempirical approximation, Eq. (2.2),

$$E_{12} = \langle h_{1A} | H | h_{2B} \rangle \approx F_\beta S_\sigma E_1. \quad (3.15)$$

Now a chain state of type  $x$  can be constructed by a linear combination of the basis orbital  $\phi$  of type  $x = \alpha, \beta, \rho, \tau$  or the equivalent lone pairs  $h_3$  and  $h_4$ :

$$\Psi_x = \sum_{n=1}^N C_n \phi_{xn}. \quad (3.16)$$

In the first-order approximation, the interactions between basis orbitals of different energies are neglected.

The coefficient  $C_n$  and the energies  $E$  of the state  $\Psi_x$  can be obtained from the solutions of the secular equation

$$\sum_{n=1}^N (H_{mn} - S_{mn} E) C_n = 0, \quad (3.17)$$

where  $S_{mn}$  is the overlap integral and  $H_{mn}$  is the Hamiltonian matrix element between the basis orbital  $\phi_m$  and  $\phi_n$ . The off-diagonal elements of the Hamiltonian matrix are given by

$$H_{mn} = F_c S_{mn} E_x, \quad m \neq n. \quad (3.18)$$

As the number of atoms (or bonds)  $N$  increases, the maximum and the minimum values of  $E$  quickly approach the values which determine the band edges and the bandwidth for an infinite chain.

Figure 3(a) shows the results of calculations for  $\alpha, \beta, \tau$ , and  $\rho$  bands. Cusachs's formula, Eq. (2.10), has been used for the parameters  $F_\beta$  and  $F_c$  in Eqs. (3.15) and (3.18), respectively. It can be seen that with  $N \geq 18$  the approach to the limiting values is quite complete. In the following discussion the results obtained with  $N = 24$  will always be used.

If instead of the  $\rho$  and  $\tau$  bases, the equivalent lone pairs are used, the combinations of  $h_3$  and  $h_4$  from all the atoms have to be considered, since the two bases are degenerate. The dimension of the secular determinant is 48 for  $N = 24$ . When the atomic  $s$  and  $p$  orbitals are used directly as the bases for the chain states, the dimension of the secular determinant for the  $p$  states is  $3N$ . The results of these calculations are shown in Figs. 3(b) and 3(c) for  $N = 24$  and 18, respectively.

Values of overlap integrals up to the third nearest neighbors are given in Table I.

In the calculation with  $\alpha, \beta, \tau$ , and  $\rho$  as bases and Cusachs's  $F$  value [Fig. 3(a)], at  $N = 24$  the band gap (between the occupied  $\rho, \beta, \tau$ , and the empty  $\alpha$  band) is about 2 eV, in good agreement with the experimental value for amorphous Se.<sup>7</sup> However, the total width of the valence bands ( $\rho$ ,

TABLE I. Overlap integrals.

	Nearest neighbor	Second neighbor	Third neighbor
$\langle \alpha   \alpha' \rangle$	0.0686	-0.0171	0.0011
$\langle \beta   \beta' \rangle$	0.0066	0.0218	0.0447
$\langle h_3   h_3' \rangle$	-0.0335	-0.0318	0.0052
$\langle h_3   h_4' \rangle$	0.0724	0.0073	-0.0059
$\langle h_4   h_3' \rangle$	-0.0795	0.0422	0.0001

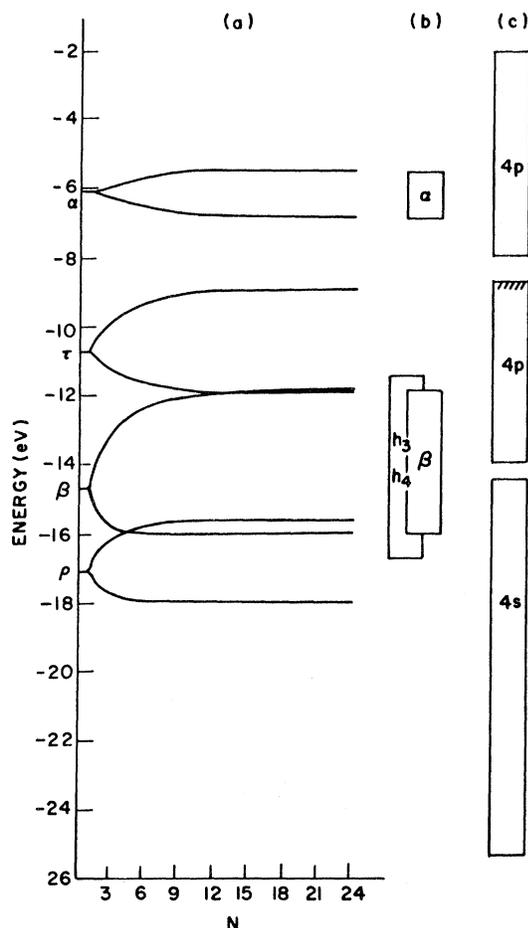


FIG. 3. Selenium-chain-state energies. (a)  $\alpha$ ,  $\beta$ ,  $\tau$ ,  $\rho$  as bases, extreme values as a function of  $N$ , the number of atoms in a chain; (b)  $\alpha$ ,  $\beta$  and the two equivalent lone pairs  $h_3$ ,  $h_4$  as bases,  $N=24$ ; (c) atomic 4s, 4p orbitals as bases,  $N=18$ .

$\beta$ , and  $\tau$ ) exceeds 9 eV, which is about 50% larger than that determined by Nielsen<sup>8</sup> with vacuum-photoemission technique.

With the equivalent lone pairs  $h_3$  and  $h_4$  replacing the  $\rho$  and  $\tau$  bases and the same formula for  $F$  [Fig. 3(b)], the total width of the valence band reduces to 5.1 eV, in better agreement with Nielsen's result. However the band gap becomes too large (4.5 eV).

Because of the large overlap between the two bonding hybrids ( $S_o = 0.515$ ), the energies  $E_\alpha$  and  $E_\beta$ , and therefore, the positions of the  $\alpha$  and  $\beta$  bands, are very sensitive to the  $F_b$  values chosen. This is illustrated by the results of calculations shown in Fig. 4. In these calculations we vary the  $F_b$  value in Eq. (2.15) from 1.3 to 1.5 while keeping the  $F_c$  value fixed to 2.0 (which differ from Cusachs's formula by < 5%, since all the overlap integrals are less than 0.1). It can be seen that with  $F_b = 1.30 \sim 1.35$ , about 10% smaller than the

Cusachs value, both the band gap and the valence-band width are in good agreement with the experimental values. The individual bandwidths obtained with  $F_c = 2.0$  differ from those obtained with the Cusachs formula by about 0.1 eV or less.

The results of the calculation with the atomic  $s$  and  $p$  orbitals as bases, Fig. 3(c), is obviously unrealistic. Not only the width of the valence band is too large but also the gap between the occupied and the empty states is too small.

#### IV. MOLECULAR ORBITALS OF Se RING

The molecular-orbital calculations of an eight-membered puckered ring have been discussed in detail in a previous publication on sulfur.<sup>10</sup> The same method is now applied to the  $\text{Se}_8$  ring molecule with the following two refinements: (i) The interactions between atoms are extended to the third neighbors (only to next nearest neighbor in the sulfur calculation); (ii) the off-diagonal element

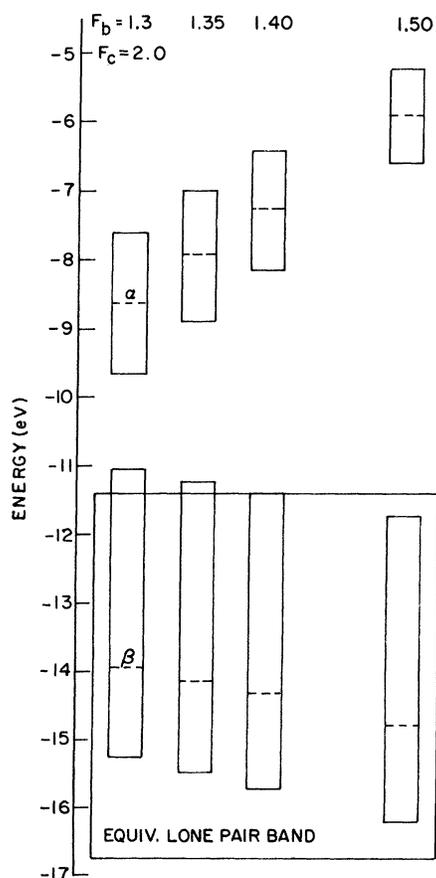


FIG. 4. Selenium-chain-state energies, with  $\alpha$ ,  $\beta$ ,  $h_3$ , and  $h_4$  as bases for different values of  $F_b$ , Eq. (2.15), and  $F_c = 2.0$ . The dashed lines in the boxes represent the positions of  $\alpha$  and  $\beta$  orbital energies at corresponding  $F_b$  values.

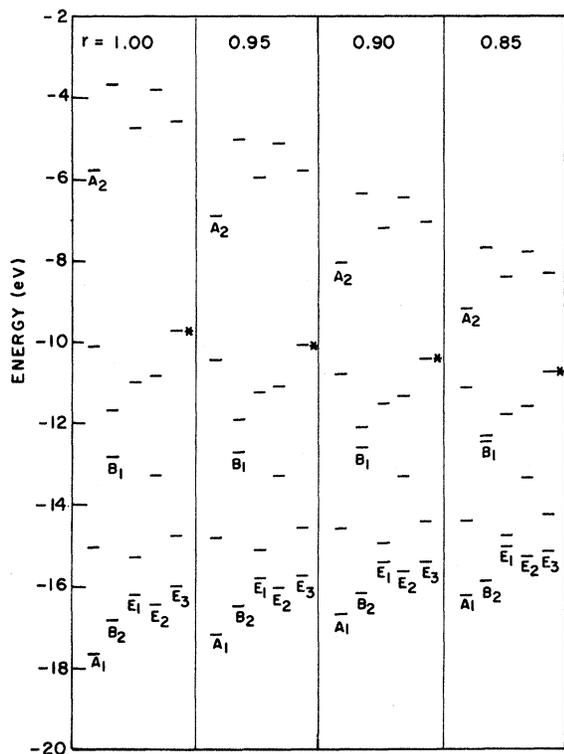


FIG. 5. Molecular-orbital energies of  $\text{Se}_8$  ring, for different values of  $F_r$ , Eq. (4.1). The energy levels of the same irreducible representations are shown in the same column, except those of  $A_2$  and  $B_1$ , which are shown in the columns of  $A_1$  and  $B_2$ , respectively. The highest occupied level is designated with a star (\*).

parameter  $F$  of Eq. (2.2) is represented by a modified Cusachs formula:

$$F_r = r(2 - |S|), \quad (4.1)$$

where  $r$  is a correction factor whose value is varied from 0.85 to 1.0.

Because of the different bond length and bond angle, the hybrid orbitals for  $\text{Se}_8$  are slightly different from those of  $\text{S}_8$  or of the Se chain, Eqs. (3.3) and (3.4). However, the symmetry-adapted combinations of hybrid orbitals given in Table I of Ref. 10 are applicable as well to  $\text{Se}_8$  (with different normalization factors due to different overlaps). The hybrid orbitals for  $\text{Se}_8$  rings are

$$h_{1,2} = 0.457s + 0.293\xi \pm 0.707\eta - 0.453\zeta, \quad (4.2)$$

$$h_3 = 0.540s + 0.842\xi, \quad (4.3)$$

$$h_4 = 0.540s - 0.346\xi + 0.768\zeta, \quad (4.4)$$

where  $h_1$  and  $h_2$  are the bonding and  $h_3$  and  $h_4$  are the lone-pair hybrids, and the coordinates  $\xi$ ,  $\eta$ ,  $\zeta$  are defined in Ref. 10 and shown in Fig. 2.

The resulting MO energy levels for  $r=0.85$  to 1.0 are shown in Fig. 5.

## V. DISCUSSION

In order to compare the calculations of Secs. III and IV with the experimental results the effects of disorder and of interaction between chains and rings have to be considered. Both effects result in the shifting of the energy levels previously calculated, and therefore it is appropriate as a first approximation to represent the effects of disorder and interchain (ring) interaction by imposing a Gaussian distribution on each of the discrete levels. Thus, the density of states at energy  $E$  can be written as

$$D(E) = N \sum_i (1/\sqrt{\pi}\omega_i) \exp[-(E - E_i)^2/\omega_i^2], \quad (5.1)$$

where  $N$  is the normalization factor, and  $\omega_i$  is the width of the Gaussian distribution associated with the discrete level  $E_i$ . Since it is best to keep the number of parameters in the semiempirical theory to a minimum, all  $\omega_i$  are assumed to be the same. Figure 6 shows the density of states for Se chains calculated with the discrete levels obtained in Sec. III with  $F_b = 1.35$  and  $F_c = 2.0$ . The density and energy are normalized such that the upper valence-band peak coincides in density and energy with that of Nielsen's<sup>8</sup> experimental curve, which is also shown in Fig. 6. With  $\omega = 0.5$  eV, excellent agreement in the positions of the minimum (near  $E = -3$  eV), the second valence-band peak (near  $E = -4.2$  eV), and the shoulder near  $-6$  eV are obtained. The experimental curve is slightly broader than the calculated one. This difference could be removed by increasing the Gaussian width to 0.75 or 1.0 eV, but the shoulder near  $-6$  eV disappears at such high  $\omega$  values. An alternate source of the extra broadening is the ring states. Figure 7 shows the density-of-states curves for the Se ring (calculated with  $r=0.85$ ) and the Se chain (same as that of Fig. 6, except the normalization). The two curves have similar structures except a slight shift in energy, which would result in extra broadenings of the peaks when the two are superposed.

The constituents of the valence bands are resolved in Fig. 8, in which we plot the densities of states from the lone-pair states and the bonding states of the Se chain separately. It can be seen that although the lone-pair states and the bonding states contribute mostly to the upper and the lower peaks, respectively, each state also contributes considerably (30~50%) to the other peak.

The imaginary part of the dielectric function  $\epsilon_2$  calculated from reflectance spectra is related to the joint density of the initial (occupied) and the final (empty) states  $(dN/dE_{ij})$ ,<sup>16</sup>

$$\epsilon_2(E) \approx \left( \frac{\hbar^2 e^2}{mE} \right) \sum_{i,j} f_{ij} \left( \frac{dN}{dE_{ij}} \right), \quad E = E_{ij} \quad (5.2)$$

where  $f_{ij}$  is the average oscillator strength for the

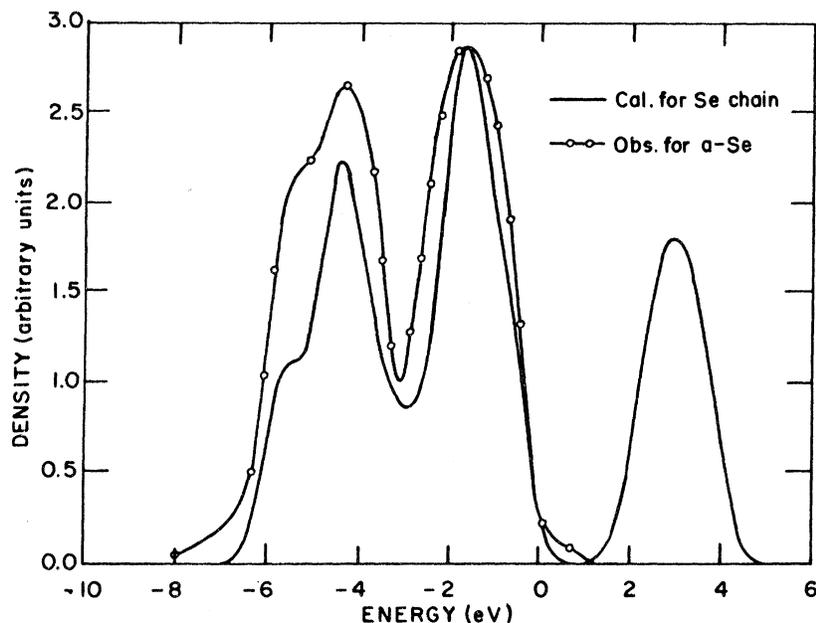


FIG. 6. Density-of-states function  $D(E)$ , Eq. (5.1), calculated for Se chain with  $F_b=1.35$ ,  $F_c=2.0$ , and  $\omega=0.5$  eV; energy and density normalized to those of experimental data for amorphous Se (Ref. 8).

interband transition ( $i \rightarrow j$ ). Let us define the function  $Z(E)$  by

$$Z(E) = \frac{1}{E} \int_{\text{VB}} D(x)D(x+E)\delta_{x+E, \text{CB}} dx, \quad (5.3)$$

where  $D(x)$  is the density-of-states function defined in Eq. (5.2);  $\delta_{x+E, \text{CB}}=1$  if  $x+E$  is in the empty states (conduction band,  $-10$  to  $-5$  eV, Fig. 7),  $=0$  otherwise; and the integration is taken over the

$x$  values corresponding to the occupied states (valence band,  $-18$  to  $-10$  eV, Fig. 7). If we assume that in an amorphous solid the oscillator strengths  $f_{ij}$  for all transitions are nearly the same, the  $E$  dependence of  $Z$  should simulate that of  $\epsilon_2$ . In Fig. 9, we plot the function  $Z(E)$  for the Se chain and ring calculated from the densities of states  $D(x)$  of Fig. 7. The  $\epsilon_2$  curves for amorphous Se<sup>7</sup> reported by Leiga and by Stuke are also shown on Fig. 9. Although it is not expected that there

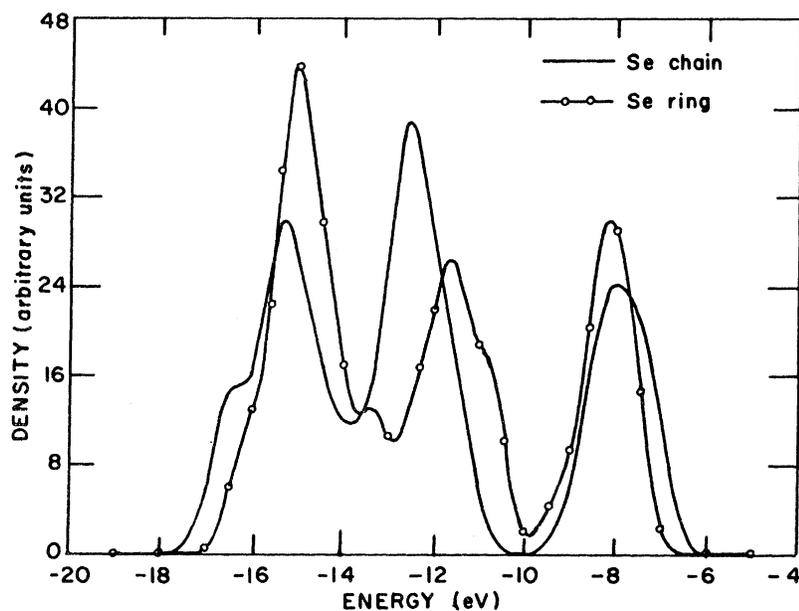


FIG. 7. Density-of-states functions  $D(E)$ , Eq. (5.1), calculated for Se chain ( $F_b=1.35$ ,  $F_c=2.0$ ) and Se ring ( $F_r=0.85$ ) with  $\omega=0.5$  eV.

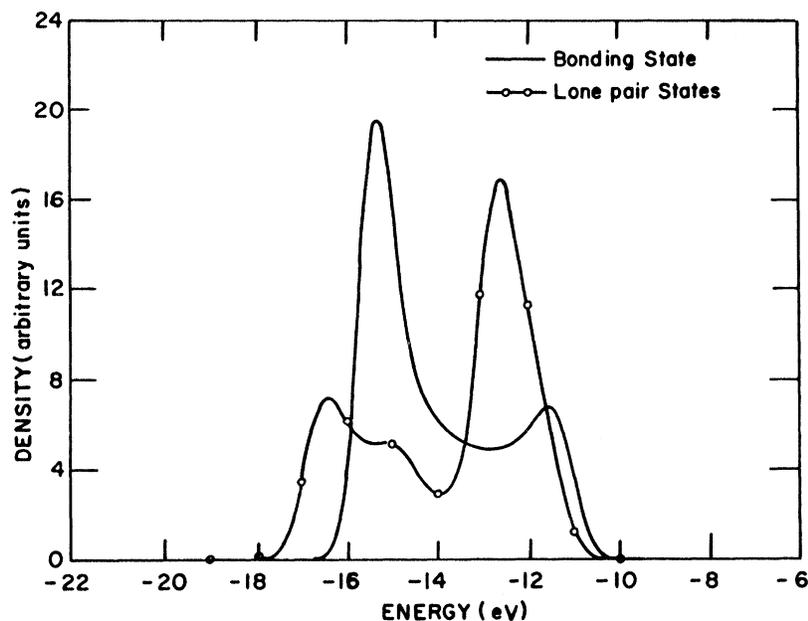


FIG. 8. The bonding states and the lone-pair states components of the valence-band density of states, Eq. (5.1), calculated for Se chain with  $F_b=1.35$ ,  $F_c=2.0$ , and  $\omega=0.5$  eV.

is perfect agreement between the  $Z$  and  $\epsilon_2$  curves, the calculated  $Z(E)$  curves do show resemblances to the experimental  $\epsilon_2$  curves, e. g., the double peaks. The shoulder in Stuke's  $\epsilon_2$  curve near 3 eV could be due to the ring component. At the high-energy end,  $\epsilon_2$  decays much slower than  $Z(E)$ . This can be attributed to the extra contributions to  $\epsilon_2$  from transitions to higher conduction states (e. g., 5s), which are not included in the present calculation. It has been suggested<sup>11</sup> that the first (lower energy) peak in the  $\epsilon_2$  spectrum arises from

transitions from the lone-pair band to the anti-bonding band, while the second peak results from those from the bonding band to the antibonding band. In Fig. 10, the contributions to  $Z(E)$  from the lone-pair band and from the bonding band are resolved for the Se chain. It can be seen that the lone-pair band contributes dominantly to the first peak, while the bonding band contributes almost equally to both peaks. It is not correct to assign the double peaks in the valence-band density of states (Figs. 7 and 8) and in the  $\epsilon_2$  spectrum to the

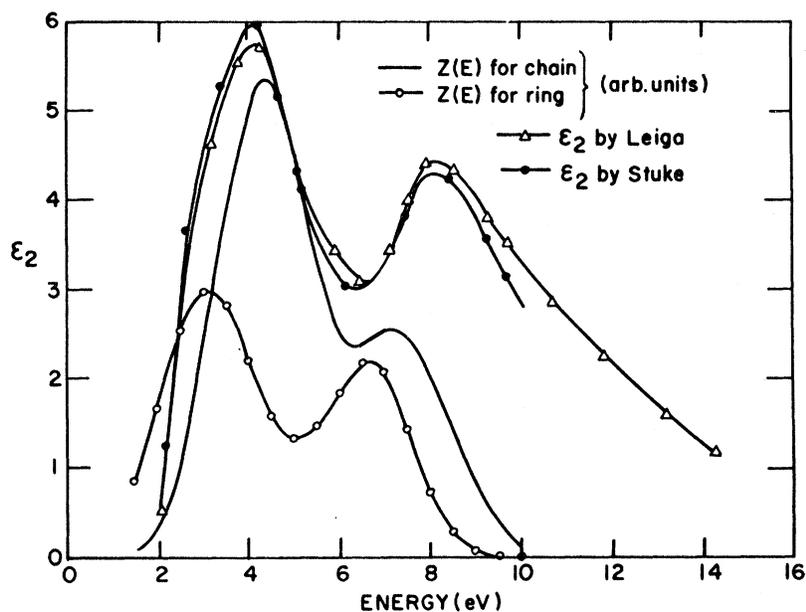


FIG. 9. The joint density-of-states functions  $Z(E)$ , Eq. (5.3), for Se chain and ring calculated from the  $D(E)$  functions of Fig. 7. Experimental data for  $\epsilon_2$  (Ref. 7) are also shown.

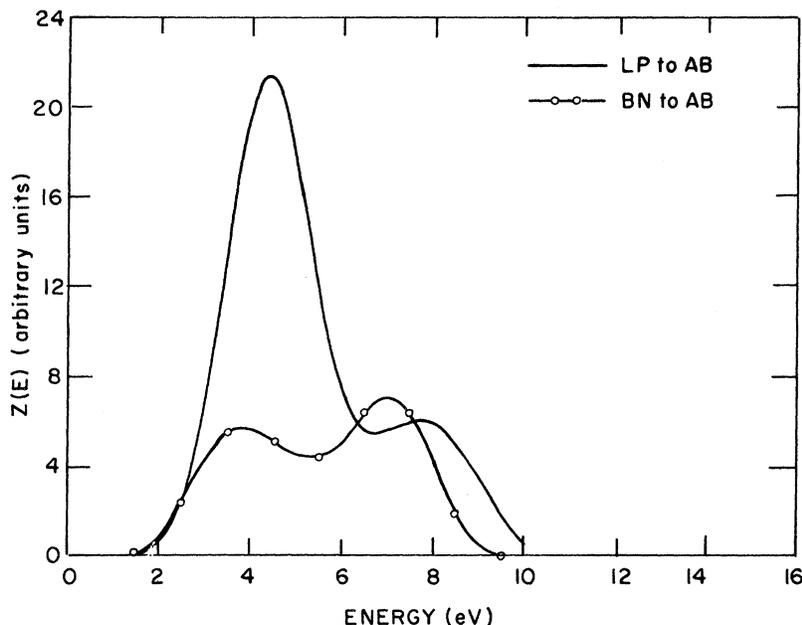


FIG. 10. The contributions to  $Z(E)$ , Eq. (5.3), for the Se chain from the transitions of (1) lone-pair states (LP) to antibonding states (AB), and (2) bonding states (BN) to AB.

lone-pair band and the bonding band separately. Rather, the double peaks arise from the interaction between the neighboring bonding orbitals,  $\beta$  of Eq. (3.5) [or the neighboring lone-pair orbitals  $h_{3,4}$  of Eq. (3.4)], resulting in a bonding and an antibonding combination of the bases. It happens that the energy of the bonding combination of  $\beta$  differs only slightly from that of lone-pair orbitals, the two bands overlap, forming the lower peak in the valence-band density of states. The overlap of the antibonding combinations of  $\beta$  and of lone pairs results in the upper peak.

In summary we have demonstrated that the semi-empirical molecular-orbital method with appropriate choices of the bases and the off-diagonal element parameter  $F$  can describe the electronic states of amorphous molecular solids in good agreement with both photoemission and optical experiments. The hybrid orbitals are shown to be a good representation for the anisotropy of the bonding in Se. The value of the parameter  $F$  calculated from Cusachs's formula is found to be slightly (10~15%) too large where the overlap integral is large (0.3~0.5).

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