PHYSICAL REVIEW B VOLUME 12, NUMBER 4 15 AUGUST 1975

Band structure and charge-density calculations for $(SN)_x$ chains

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(Received 5 May 1975)

We present the results of linear-combination-of-atomic-orbitals calculations for the electronic structure of polysulfurnitride chains with three different planar structures, one with one molecule per unit cell and two with two molecules per unit cell each. In all cases, the calculations yield two overlapping bands at the Fermi level: a σ band of metallic character, and a π band. The π states are mostly localized at the sulfur atoms, and contain only a small number of electrons. Band structures and densities of states at the Fermi level are displayed. The picture of overlapping bands seems to explain satisfactorily the experimental observations.

I. INTRODUCTION

Recent experiments on the properties of polysulfurnitride[1–4] have raised considerable interest in the structure and properties of this one-dimensional crystal. These experiments found that $(SN)_x$ exhibited a metallic ground state. The measurements of conductivity and Seebeck coefficients[1] indicate that, unlike the case of other one-dimensional metallic chains,[5] there is no metal-insulator transition at low temperatures.

Other experiments[2,3] support these conclusions. Specific-heat measurements in the 1.5–10 °K temperature range found a linear temperature contribution, which can be interpreted as arising from a one-dimensional conduction band with an electron density of states of 0.18 state/(eV spin molecule) at the Fermi energy.[2] The measurements also suggest a weak interchain coupling.

The optical measurements[3] show a metal-like reflectance in a range from the infrared through the near ultraviolet region with a well-defined plasma edge at 4500 Å.

The measurements of conductivity at very low temperature led to the discovery of superconductivity,[4] with a transition temperature in the neighborhood of 0.26 °K.

Although $(SN)_2$, $(SN)_4$, etc., have been of interest to chemists[6] and their structures have been analyzed carefully, there is no corresponding analysis of $(SN)_x$ polymers. These analyses indicate that in compounds such as $(SN)_2$, $(SN)_4$, etc., which are not planar molecules, the angle between bonds at each sulfur atom is in the neighborhood of 100° and, at the nitrogen atom, it is in the neighborhood of 120°.

The structure of polysulfurnitride has been a matter of considerable controversy. Early x-ray analysis of $(SN)_x$ indicated that it is a planar zig-zag chain with atoms arranged in the form of N-S-N-S. The bonds between nitrogen and sulfur atoms were thought to be equivalent, i.e., resonant hybrids between single and double bonds.[7,8] However, subsequent electron diffraction analysis[1,9] suggested that $(SN)_x$ has alternating bonds with bond lengths of 1.55 and 1.73 Å. The angles at the nitrogen and sulfur atoms were quoted at 108° and 119°, respectively. This structure is not internally consistent, since $(SN)_x$ is believed to be a linear zig-zag chain, but the reported angles at the nitrogen and sulfur atoms are not equal.

If we wish to assume a linear structure with one SN molecule per unit cell, the S-N and N-S bond lengths are arbitrary, but the angles at the sulfur and at the nitrogen atoms should be equal. For example, a choice of bond lengths of 1.55 and 1.73 Å and an angle of 113.5° (average between the two reported angles) results in the structure shown in Fig. 1(a).

Recent electron-diffraction analysis showed[10] a more complex structure with the unit cell containing two SN molecules along the chain. The SN bond lengths are alternately 1.58 and 1.72 Å, and the angles at nitrogen and sulfur atoms are seen to be 113.5° and 111.5°. This structure is shown in Fig. 1(b).

Lately,[11] a third structure, similar to the one above but with slightly different bond lengths and angles, has been claimed to be the structure of $(SN)_x$. This structure is shown in Fig. 1(c).

For all cases in Fig. 1, we present an *ab initio* linear-combination-of-atomic-orbitals (LCAO) calculation of the band structure of $(SN)_x$ polymers.

Section II deals with our approach to the problem and the method of calculation. In Sec. III we present the results of our calculations, both for the SN molecules and $(SN)_x$ polymers. In Sec. IV we discuss our results and compare them with existing experimental data.

II. CALCULATION

The method used is the simple-linear-combination-of-atomic-orbitals (LCAO).[12,13] First we calculate the energy levels of the diatomic SN molecule at various S-N separations.

The atomic orbitals used are the $2s$, $2p_x$, $2p_y$, $2p_z$ of nitrogen and the $3s$, $3p_x$, $3p_y$, $3p_z$ of sulfur,

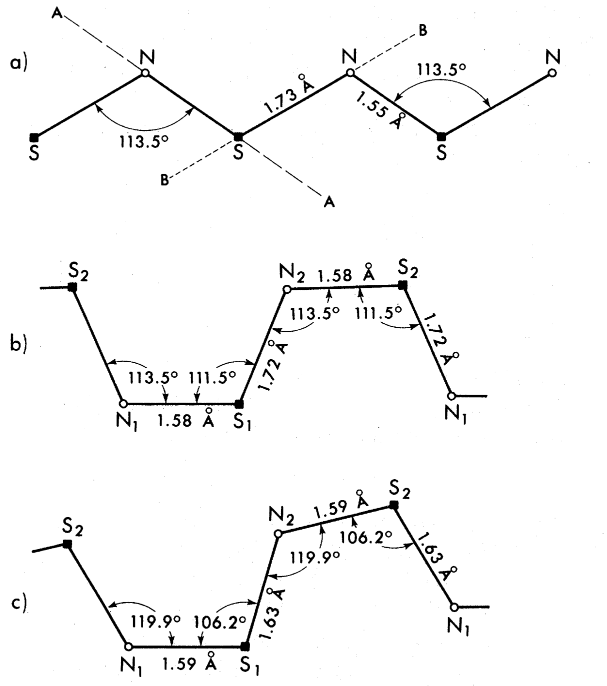

FIG. 1. Various chain structures used in our band-structure calculations. (a) One SN molecule per unit cell, (b) and (c) two SN molecules per unit cell (based on recent electron-diffraction studies).

since these are the valence orbitals of the respective atoms.

If nitrogen is taken to be at the origin and sulfur at $\vec{\tau}$, then

$$\phi(\vec{r})=\sum_{i=1}^{4}\alpha_i\,\chi_i(\vec{r})+\sum_{i=5}^{8}\alpha_i\,\chi_i(\vec{r}-\vec{\tau})\ , \tag{1}$$

where $\phi(\vec{r})$ is the molecular orbital of an electron in the SN molecule and the α_i's are variational parameters. The symbols χ_i, $i=1,\ldots 8$, denote the eight atomic orbitals N_{2s}, N_{2p_x}, N_{2p_y}, N_{2p_z}, S_{3s}, S_{3p_x}, S_{3p_y}, and S_{3p_z}.

The actual forms of the atomic orbitals are taken from self-consistent-field atomic calculations,[14] where they are expressed as linear combinations of Slater-type orbitals.

The Hamiltonian used in the case of the molecules is

$$H=H_{\mathrm{KE}}+U_{\mathrm{N}}(\vec{r})+U_{\mathrm{S}}(\vec{r}-\vec{\tau})+H_{\mathrm{AE}}\ . \tag{2}$$

The term H_{KE} is the kinetic energy of the electron, U_{N} and U_{S} are the screened potentials of the nitrogen and sulfur, respectively, and H_{AE} is the atomic exchange term.

The screened, spherically symmetric potentials U_{N} and U_{S} are determined by solving Poisson's equation

$$\nabla^2 U=4\pi\rho\ . \tag{3}$$

Here, $\rho(\vec{r})$ is the charge density around the atom, given by

$$\rho(\vec{r})=2Z\delta(\vec{r})-2\sum n_i\,|\chi_i^{(0)}(\vec{r})|^2\ , \tag{4}$$

where n_i denotes the occupation number of the orbitals, the sum being carried over all core and valence orbitals of the atom. In (4), $\chi_i^{(0)}(\vec{r})$ denotes the radial part of the orbital wave function. The factor of 2 comes from our choice of atomic rydberg units such that $\hbar=1$, $m=1/2$, and $e^2=2$.

The boundary conditions are $rU(r)\to 0$ as $r\to\infty$ and $rU(r)\to -2Z$ as $r\to 0$.

The last term in (2), H_{AE}, is defined such that

$$[H_{\mathrm{KE}}+U_{\mathrm{N}}(\vec{r})+H_{\mathrm{AE}}]\,|\chi_i(\vec{r})\rangle=E_i\,|\chi_i(\vec{r})\rangle \tag{5}$$

when $i=N_{2s}$, N_{2p_x}, N_{2p_y}, and N_{2p_z};

$$[H_{\mathrm{KE}}+U_{\mathrm{S}}(\vec{r}-\vec{\tau})+H_{\mathrm{AE}}]\,|\chi_i(\vec{r}-\vec{\tau})\rangle=E_i\,|\chi_i(\vec{r}-\vec{\tau})\rangle \tag{6}$$

when $i=S_{3s}$, S_{3p_x}, S_{3p_y}, and S_{3p_z}. Here, E_i denotes the atomic orbital energies.

It follows from the standard LCAO techniques that the orbital energies of the SN molecule $E^{(u)}$, $u=1,\ldots,8$, are the eigenvalues of the matrix equation.

$$\sum_j H_{ij}\,\alpha_j^{(u)}=E^{(u)}\sum_j S_{ij}\,\alpha_j^{(u)} \tag{7}$$

Here H_{ij} is the Hamiltonian, S_{ij} is the overlap matrix, and the $\alpha_j^{(u)}$'s are the coefficients defined in Eq. (1).

The off-diagonal matrix elements of the overlap matrix S are as large as 0.45 in some cases, due to the small interatomic distances (1.5–1.75 Å); therefore, they cannot be neglected.

Since χ_i and χ_j are eigenstates of the atomic Hamiltonian [Eqs. (5) and (6)], with the use of Eqs. (1), (2), (5), and (6), the molecular Hamiltonian can be expressed as a function of the overlap matrix S_{ij}, the screened atomic potential matrices $U_{\mathrm{N}_{ij}}$ and $U_{\mathrm{S}_{ij}}$, and the atomic energy levels E_i. It is now possible to evaluate the matrix elements in Eq. (7) and hence the eigenvalues $E^{(u)}$. This procedure was followed for two SN molecules with bond lengths of 1.55 and 1.73 Å, respectively.

The preliminary model of polysulfurnitride [shown in Fig. 1(a)] can be considered to be a chain of SN molecules at a distance a (2.74 Å) apart. Thus, the Bloch function is

$$\psi(\vec{r})=\sum_{n=-\infty}^{\infty}e^{ikna}\,\phi(\vec{r}-na) \tag{8}$$

where $\phi(\vec{r})$ is given by Eq. (1). The total Hamiltonian is

$$H=H_{\mathrm{KE}}+H_{\mathrm{AE}}+\sum_{n=-\infty}^{\infty}[U_{\mathrm{N}}(\vec{r}-na)+U_{\mathrm{S}}(\vec{r}-\vec{\tau}-na)] \tag{9}$$

Again, from LCAO it follows that

$$\sum_j H_{ij}(k)\,\alpha_j^{(u)}(k) = E^{(u)}(k) \sum_j S_{ij}(k)\alpha_j^{(u)}(k) \qquad (10)$$

where u denotes the band index and k the wave vector.

As before, the Hamiltonian H_{ij} can be expressed as a function of the overlap matrix S, the matrices of the screened atomic potentials U_N and U_S, and the atomic orbital energies E_i.

The matrix elements of S, U_N and U_S are themselves linear combinations of two center integrals of the form

$$S_{ij}(k) = \langle \chi_i(\vec{r}) | \chi_j(\vec{r})\rangle + e^{ika}\langle \chi_i(\vec{r}) | \chi_j(\vec{r} - a)\rangle + e^{-ika}\langle \chi_i(\vec{r}) | \chi_j(\vec{r} + a)\rangle + \cdots . \qquad (11)$$

The calculation was first carried out in the nearest-neighbor approximation; that is, only those two-center integrals with separation of 1.55 and 1.73 Å were considered. A second calculation which included next-nearest neighbors was also carried out. In this case, the largest matrix elements neglected were three-center integrals of the form

$$\langle \chi_N(\vec{r}) | U_S(\vec{r} - \vec{\tau}) | \chi_N(\vec{r} - a)\rangle$$

and these were estimated to be of the order of a few hundredths of a rydberg.

The band structure of the second model of $(SN)_x$, shown in Fig. 1(b), is also calculated. Here, we have to consider two SN molecules per unit cell; therefore, we have to consider linear combinations of sixteen orbitals. Hence,

$$\phi(\vec{r}) = \sum_{i=1}^{4} \alpha_i \chi_i(\vec{r}) + \sum_{i=5}^{8} \alpha_i \chi_i(\vec{r} - \vec{\tau}_{S1}) + \sum_{i=9}^{12} \alpha_i \chi_i(\vec{r}_i - \vec{\tau}_{N2}) + \sum_{i=13}^{16} \alpha_i \chi_i(\vec{r} - \vec{\tau}_{S2}) \qquad (12)$$

where we have assumed that the unit cell is of the form $(N_1S_1N_2S_2)$ with position vectors of the atoms being

$\vec{\tau}_{N1} = (0, 0, 0)$

$\vec{\tau}_{S1} = (1.58, 0, 0)$

$\vec{\tau}_{N2} = (2.21, 1.60, 0)$

$\vec{\tau}_{S2} = (3.79, 1.66, 0)$

in Ångstrom units.

The Bloch function is again given by Eq. (8) but with $a = 4.48$ Å. The Hamiltonian is

$$H = H_{KE} + H_{AE} + \sum_{n=-\infty}^{\infty} [U_N(\vec{r} - na) + U_{S1}(\vec{r} - na - \vec{\tau}_{S1}) + U_{N2}(\vec{r} - na - \vec{\tau}_{N2}) + U_{S2}(\vec{r} - na - \vec{\tau}_{S2})] . \qquad (13)$$

We again arrive at equation of the form of Eqs. (10) and (11).

In this case, we considered all the two-center integrals up to and including 4.14 Å, i.e., up to third-nearest neighbors. The largest matrix elements neglected were the three-center integrals of the form $\langle \chi_{N1} | U_{S1} | \chi_{N2}\rangle$; these were estimated to be a few hundredths of a rydberg.

The above procedure was repeated for the third structure shown in Fig. 1(c). In this case,

$\vec{\tau}_{N1} = (0, 0, 0)$

$\vec{\tau}_{S1} = (1.59, 0, 0)$

$\vec{\tau}_{N2} = (2.04, 1.57, 0)$

$\vec{\tau}_{S2} = (3.59, 1.94, 0)$

in Ångstrom units and $a = 4.43$ Å.

Equations (10)–(13) still hold, and the approximations made are the same as above.

III. RESULTS

The atomic energy levels were obtained from the tables[14] and are shown in Fig. 2. Our results for the energy levels of the SN molecules are also shown in Fig. 2. We give the results for SN molecules with S–N bond lengths of 1.73 and 1.55 Å, corresponding to the two bond lengths in the preliminary model of the $(SN)_x$ polymer. It is seen that the SN molecule has two doubly degenerate π levels and four σ levels, as required by symmetry. The occupancy of each level is also indicated.

The results of the calculation of the energy bands for the preliminary model of the $(SN)_x$ polymer are shown in Fig. 3. Figure 3(a) gives the energy bands in the nearest-neighbor approximation, and Fig. 3(b) shows the corresponding curves when the next-nearest neighbors are considered. The Fermi

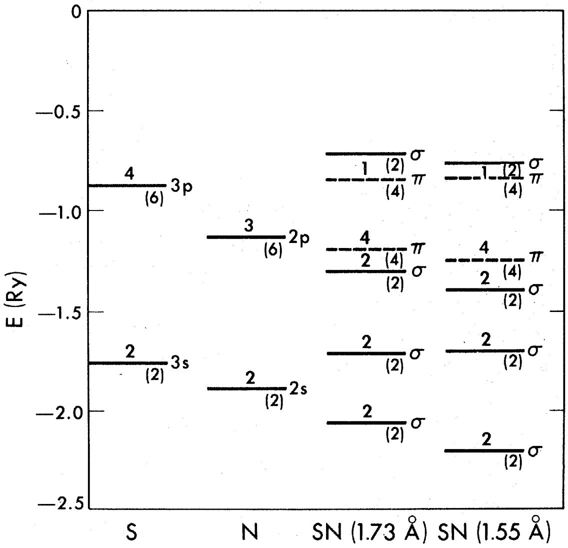

FIG. 2. Atomic- and molecular-energy orbital levels of the sulfur atom, the nitrogen atom, and the SN molecule, with interatomic separations of 1.73 and 1.55 Å.

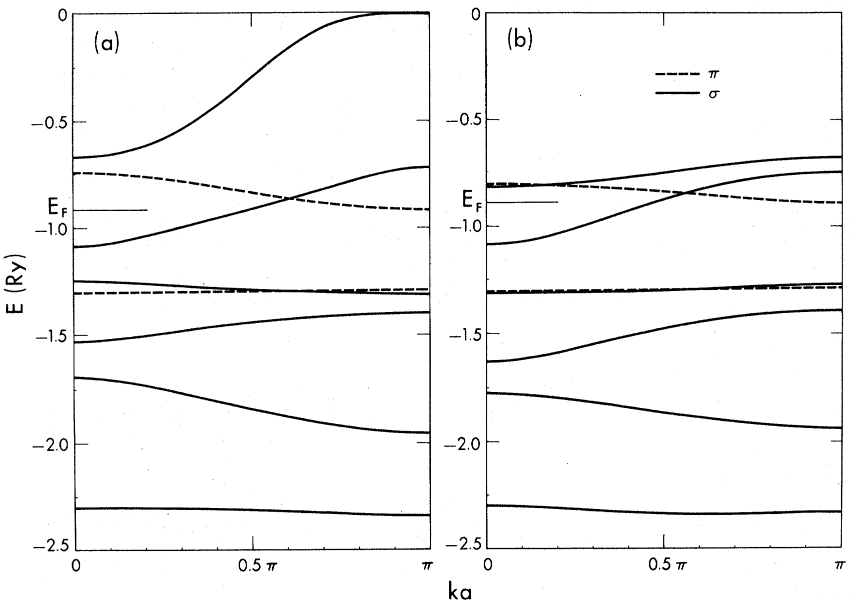

FIG. 3. Band structure of the $(SN)_x$ polymer for the structure of Fig. 1(a), with one SN molecule per unit cell (a) in the nearest-neighbor approximation, and (b) in the next-nearest-neighbor approximation.

level is shown in both cases. We see from the figure that there are six σ bands and two π bands, as expected from symmetry considerations.

There are two overlapping bands at the Fermi level, the fifth σ band and the second π band. The σ band crosses the Fermi level close to its middle point at $ka=\frac{1}{2}\pi$; the π band has its bottom at $ka=\pi$, very close to but slightly below the Fermi energy. The π states at the Fermi level, as shown in Fig. 4, correspond to electronic charge densities predominantly localized at the sulfur atoms. The σ states, on the other hand, displayed in Fig. 5, are extended states of metallic character equally distributed among sulfur and nitrogen atoms. Figures 4 and 5 show contours of charge densities in three planes: (i) the plane of the chain (only for σ bands); (ii) a plane perpendicular to (i) which contains a 1.55-Å S-N bond; and (iii) a plane perpendicular to (i) which contains 1.73-Å S-N bonds.

The results of the calculation of the energy bands for the models of $(SN)_x$, given by Figs. 1(b) and 1(c), are shown in Figs. 6(a) and 6(b). It is seen that in essential details these band structures do not differ from the ones in Fig. 3. There are sixteen bands now, twelve σ bands and four π bands. The unit cell is twice as large, and the Brillouin zone correspondingly twice as small. Furthermore, the bands we get do not differ significantly from the ones obtained from Fig. 3 by folding the bands over at $ka=\frac{1}{2}\pi$, which would be the case when the unit cell doubles in size.

It is worth pointing out that the structures of Figs. 1(b) and 1(c) lead to bands which are degenerate at the zone boundary. This is due to an extra hidden symmetry in the Hamiltonian which has been discussed before.[15] Owing to this sticking together of the bands, the similarity between the bands in Fig. 6 and those of Fig. 3—folded in half—is much more apparent. The overlap between σ and π bands is maintained in the new structures, but the Fermi level now falls close to the origin for the π band, and close to the zone boundary for the σ band.

IV. DISCUSSION AND CONCLUSIONS

Our main result is the fact that two overlapping bands (one σ, one π) coexist at the Fermi level. Such a result can explain various properties of $(SN)_x$:

(1) Since no band is exactly half-filled, the tendency for a Peierls instability to occur is very much diminished.

(2) The two-band overlap explains in a consistent way the apparent paradox of high conductivity (large bandwidth) and high linear specific heat (small bandwidth). Our calculation produces for the σ band (or double band, for the bands stick together)

$$W_\sigma = 0.336 \text{ Ry} \quad \text{for Fig. 1(a)},$$

$$W_\sigma = 0.107 \text{ Ry} \quad \text{for Fig. 1(b)},$$

$$W_\sigma = 0.154 \text{ Ry} \quad \text{for Fig. 1(c)}.$$

Corresponding density of states at the Fermi level are

$$D_\sigma(\epsilon) = 1.94 \text{ states/(Ry spin molecule) for Fig. 1(a)},$$

$$D_\sigma(\epsilon) = 4.02 \text{ states/(Ry spin molecule) for Fig. 1(b)},$$

$$D_\sigma(\epsilon) = 5.28 \text{ states/(Ry spin molecule) for Fig. 1(c)}.$$

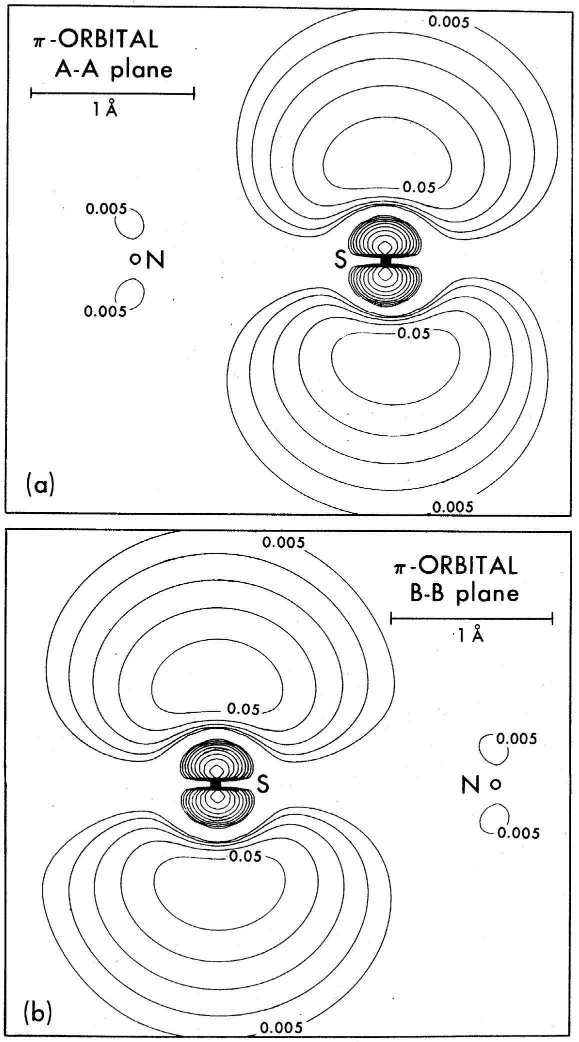

FIG. 4. Charge-density contours corresponding to the band structure of Fig. 1(a) for the second π band at the Brillouin-zone boundary, i.e., at the Fermi level. (a) the charge density in the A-A plane of Fig. 1(a), and (b) the charge density in the B-B plane. The charge-density increases by a factor of $10^{0.25}=1.78$ from one contour to the next. Thus, the contours represent charge densities of 0.005, 0.0089, 0.0158, 0.0282, 0.05, 0.089, 0.158, 0.282, 0.5....

The π bands are narrower:

$$W_\pi = 0.087 \text{ Ry} \quad \text{for Fig. 1(a)},$$

$$W_\pi = 0.099 \text{ Ry} \quad \text{for Fig. 1(b)},$$

$$W_\pi = 0.125 \text{ Ry} \quad \text{for Fig. 1(c)},$$

which, for a fractional occupation n (electrons per molecule, $n \sim 0.3$), yields

$$D_\pi(\epsilon, n) = 4.66 n^{-1} \text{ states/(Ry spin molecule)} \quad \text{for Fig. 1(a)},$$

$$D_\pi(\epsilon, n) = 4.02 n^{-1} \text{ states/(Ry spin molecule)} \quad \text{for Fig. 1(b)},$$

$$D_\pi(\epsilon, n) = 3.24 n^{-1} \text{ states/(Ry spin molecule)} \quad \text{for Fig. 1(c)}.$$

(3) The experimentally observed value for the density of states[2] of 0.18 state/(eV spin molecule), i.e., 2.45 states/(Ry spin molecule), compares reasonably well with our calculated values.

(4) Our model predicts vertical optical transi-

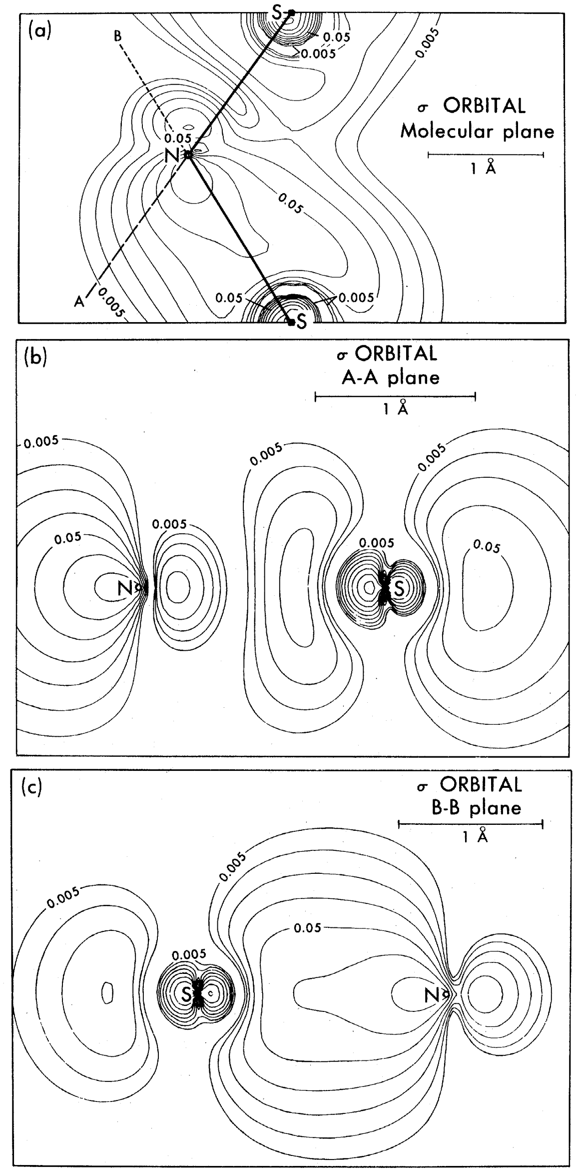

FIG. 5. Charge-density contours corresponding to the band structure of Fig. 1(a) for the σ-band at the Fermi level. (a) the charge density in the plane of the molecule, (b) in the A-A plane, and (c) in the B-B plane. The charge densities correspond to the same contours as for Fig. 4.

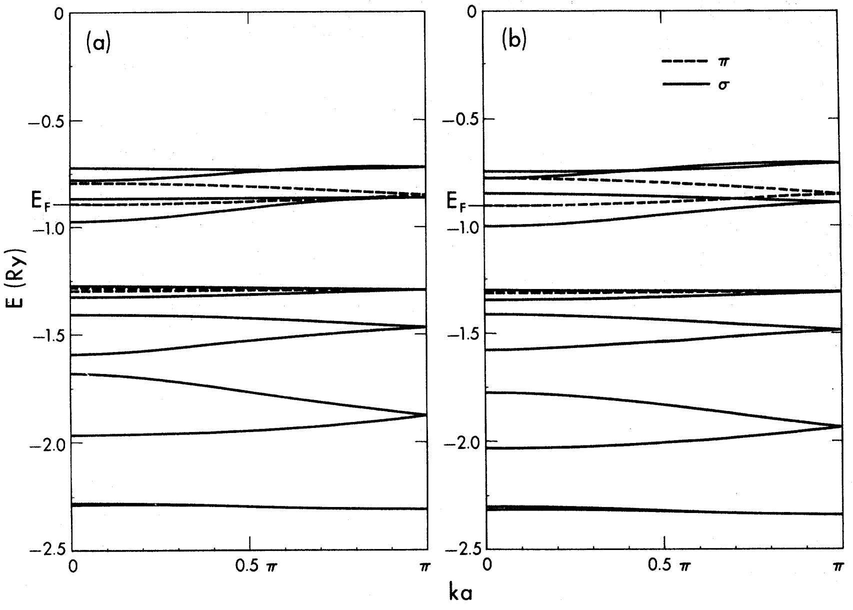

FIG. 6. Band structures for the $(SN)_x$ polymer for the cases of two SN molecules per unit cell. (a) the band structure for the model of Fig. 1(b), and (b) the band structure for the model of Fig. 1(c).

tions with the following thresholds:

(4a) (σ to π) and (π to σ) transitions, which correspond to polarization perpendicular to the plane of the chain:

$$\left.\begin{array}{ll}\sigma\rightarrow\pi & 0.05\ \text{Ry}\\ \pi\rightarrow\sigma & 0.14\ \text{Ry}\end{array}\right\}\ \text{for Fig. 1(a)},$$

$$\left.\begin{array}{ll}\sigma\rightarrow\pi & 0.02\ \text{Ry}\\ \pi\rightarrow\sigma & 0.04\ \text{Ry}\end{array}\right\}\ \text{for Fig. 1(b)},$$

$$\left.\begin{array}{ll}\sigma\rightarrow\pi & 0.04\ \text{Ry}\\ \pi\rightarrow\sigma & 0.06\ \text{Ry}\end{array}\right\}\ \text{for Fig. 1(c)}.$$

(4b) (σ to σ) and (π to π) transitions, which correspond to polarization in the plane of the chain:

$\sigma\rightarrow\sigma$ 0.12 Ry for Fig. 1(a) ,

$\sigma\rightarrow\sigma$ 0.14 Ry for Fig. 1(b) ,

$\sigma\rightarrow\sigma$ 0.17 Ry for Fig. 1(c) .

Gaps have been quoted in the literature[8] at 1.77 and 4–6 eV (0.13 and 0.30–0.45 Ry).

(5) If the structure is not planar but helical or three dimensional[10] in any other way, the σ and π states hybridize and no longer keep their character. If the hybridization is not too drastic, its main effect is to remove the degeneracies at the cross-over point, but the general shape of the bands remains essentially unchanged. In that case, only one band (a σ-π hybrid) would intersect the Fermi level at several points, but our conclusions would remain the same.

It is interesting to remark that in recent attempts to explain some properties of other linear chain solids,[16] mainly TTF-TCNQ, band structures with overlapping bands have been assumed. Our calculation produces one such cross-over picture from first principles, albeit due to different symmetry considerations.

In conclusion, we obtain an electronic structure for $(SN)_x$ which explains satisfactorily the known experimental facts. Improvement of the calculation requires better and more reliable determination of the crystal structure. With that, it could be possible to include three-dimensional effects, increase our basis set, and refine the calculation.

The recently discovered superconductivity of polysulfurnitride points out the necessity of including three-dimensional effects and, most importantly, to understand the nature and form of the lattice-vibration spectrum. These effects, again, depend crucially on an accurate and reliable determination of the crystal structure. The fact, however, that the σ-π band overlap is a common feature of all the one-dimensional structures here considered, and the fact that the closest interatomic distance between chain is estimated[10] to be 3.1 Å, suggest that the main features of our calculation should remain valid and thus play a fundamental role in all properties of $(SN)_x$.

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*Work supported in part by the National Science Foundation through Grant No. DMR72-03106-A01.

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