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Organic Conductors

Band Structure of Polyacetylene, P. M. GRANT,
IBM Research Laboratory, San Jose, CA--Using the extended
Huckel method, we have calculated the one-dimensional band
structure of polyacetylene in both cis- and trans-
isomerization. For reasonable values of alternating
carbon-carbon bond lengths, we find both structures lead
to medium band gap (~ 1.5 eV) semiconductors with fairly
wide valence and conduction bands (~ 5 eV), consistent with
reported optical properties and estimated mobilities. The
band gap in trans- $(CH)_x$ appears at the Brillouin zone
edge, while in cis- $(CH)_x$ it is at zone center. Unlike
some other semiconductors^x, such as polyethylene, the con-
duction band states in both forms are bound suggesting
that donor as well as acceptor doping is possible. Varia-
tion of the density-of-states and effective masses with
doping will be discussed on a rigid band interpretation
of the movement of the Fermi level.

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Data will be presented on the optical transmission through films of polyacetylene, $(\text{CH})_x$, in the spectral range from far infrared through visible frequencies. The effects of doping on optical properties at frequencies below the energy gap and in the vicinity of the lowest interband transition near 1.8 eV have been studied. In the far to middle ir, i. e. below 0.2 eV, a dramatic increase in the optical absorption is observed as the semiconducting $(\text{CH})_x$ is doped with iodine. The large increase in far-ir absorption which occurs near 2 mole% is interpreted in terms of a semiconductor-metal transition in the heavily doped $(\text{CH})_x$. We find no shift in the $(\text{CH})_x$ interband transition with doping. However an absorption tail develops below the gap edge leading to strong absorption throughout the ir in heavily doped material.

*Supported by ONR.

EI 9 DC Magnetic Susceptibility of $(\text{SN})_x$. C. M. BASTUSCHECK, R. A. BUHRMAN, H. TEMKIN and J. C. SCOTT, Cornell U.* -- The temperature dependence of the DC magnetization of $(\text{SN})_x$ has been investigated with a SQUID magnetometer to temperatures below 25 mK and in magnetic fields from .003 to 500 Oe. A gradual diamagnetic transition, beginning below $T = .25$ K, was observed for crystals having their fiber axis both parallel and perpendicular to the applied fields, in qualitative (1) agreement with the most recent results of Dee et al. However the results differ quantitatively. In particular, the superconducting magnetization, while increasing with applied field H up to about .5 Oe, was found to be linear in H only for $H < .04$ Oe for crystals in the perpendicular orientation. With the field parallel to the fiber axis no linear region could be identified for fields as low as .01 Oe. In the high field regime, an observable magnetization remained for fields in excess of 100 Oe.

*Research supported, in part, by NSF

(1) R. H. Dee et al., Solid State Commun., 24, 469 (1977)

EI 10 Transport Properties of Doped Polyacetylene*. R. L. GREENE, J. F. KWAK, T. C. CLARKE and G. B. STREET, IBM Research Laboratory, San Jose, CA--We report measurements on AsF_5 doped polyacetylene, $[\text{CH}(\text{AsF}_6)]_x$, of the thermoelectric power (S) from 300°K to 10°K, the electrical conductivity from 300°K to 30 mK and the magnetoresistance below 4.2°K. For a polycrystalline film with $y \sim 0.1$ the thermopower is small and positive at 300°K (~ 10 $\mu\text{V}/\text{K}$) and decreases linearly with temperature extrapolating to zero at $T=0^\circ\text{K}$. As reported recently, these films have a high room temperature conductivity (~ 1000 cm^{-1}) and a slightly activated temperature dependence [$\sigma(300\text{K})/\sigma(1\text{K}) \leq 2$ in our best films]. Below 1°K we find σ is constant and there is a small negative magnetoresistance ($\Delta\rho/\rho \sim 1\%$ for 20 kOe). No evidence of superconductivity was found down to 30mK. These results suggest that doped polyacetylene is a disordered metal or degenerate semiconductor at all temperatures. With this assumption a free electron model for $S(T)$ gives a value for the Fermi energy of $\epsilon_F = 0.9$ eV.

*Work supported in part by the ONR.

¹C. K. Chiang, et al., Phys. Rev. Letters, 39, 1098 (1977)

EI 11 Raman Scattering in Brominated $(\text{SN})_x$. H. TEMKIN, Cornell University, Ithaca, NY and G. B. STREET, IBM Research, San Jose, CA--The polarized Raman spectra of crystals of $(\text{SN Br}_3)_y$, where $.2 < y < .4$, have been measured as functions of temperature (300-2K) and laser wavelength. These spectra are compared with those of pure $(\text{SN})_x$. The energies of the two strongest Raman lines (160 and 222 cm^{-1}) observed in brominated crystals are characteristic of a particular molecular form of bromine, Br_3^- . Their polarization is consistent with a linear, asymmetric molecule oriented parallel to the $(\text{SN})_x$ chain direction. The sharpness of these Raman modes at 2K suggests a well-defined site for the bromine molecule. The resonance behavior of the spectrum further supports the Br_3^- assignment. The

Raman spectra of other materials containing Br_3^- (PyHBr and CsBr_3), showing analogous resonance behavior, will be presented.

*Supported by NSF through Cornell MSC.

EI 12 Pressure Dependence of Transport Properties in $(\text{SNBr}_{0.4})_x$ Crystals. W. D. GILL, J. F. KWAK, R. L. GREENE, K. SEEGER* and G. B. STREET, IBM Research Laboratory, San Jose, CA 95193-- The pressure dependence of normal conductivity of $(\text{SNBr}_{0.4})_x$ crystals has been measured at 300K both // and \perp to the b-axis for hydrostatic pressure up to 17 kbar. $\sigma_{//}$ increases by $\sim 1.3\%$ /kbar in sharp contrast to the $\sim 40\%$ /kbar increase observed in $(\text{SN})_x$ crystals. The observed pressure dependence can be reasonably accounted for by lattice stiffening increasing the electron-phonon scattering lifetime implying that electron-electron scattering has been suppressed by bromine treatment of $(\text{SN})_x$. Preliminary results indicate a monotonic decrease with pressure of the superconducting transition temperature T_c , an effect opposite to the pressure induced increase of T_c observed in $(\text{SN})_x$.

*Permanent address: University of Vienna and the Ludwig Boltzmann Institut für Festkörperphysik, Vienna, Austria.

EI 13 Conductivity and Hall Effect in Polyacetylene, an Organic Metal*. K. SEEGER, + W. D. GILL, T. C. CLARKE, and R. GEISS, IBM Research Laboratory, San Jose, CA 95193--In the high polymer $(\text{CH})_x$ ("polyacetylene") treated with arsenic pentafluoride the electrical conductivity and the Hall effect have been measured at temperatures between 4.2 and 350K. The Hall measurements have been done by the 2-phase-method of LUPW et al. (Review of Scientific Inst. 38 (1967) 1608). The results indicate that this material is a metal with order-of-magnitude one carrier per CH-group and a mobility dominated by hopping, possibly between $(\text{CH})_x$ chains or fibers. At temperatures somewhat below room temperature a transition is found between the low-temperature hopping to band conduction. A short-time compression of 10 kilobars increases the density of the material by a factor of 5 without changing the conductivity, however. Electron microscope pictures show microcrystals at cracks which develop in the compressed material after a few days.

+On leave of absence from the University of Vienna, and the Ludwig Boltzmann-Institute for Solid State Physics, Vienna.

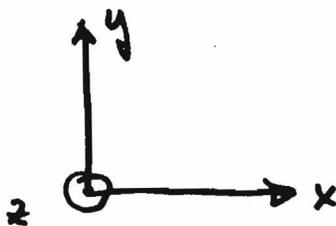
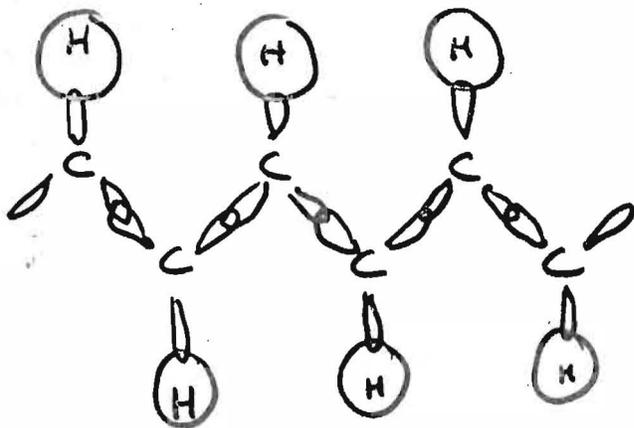
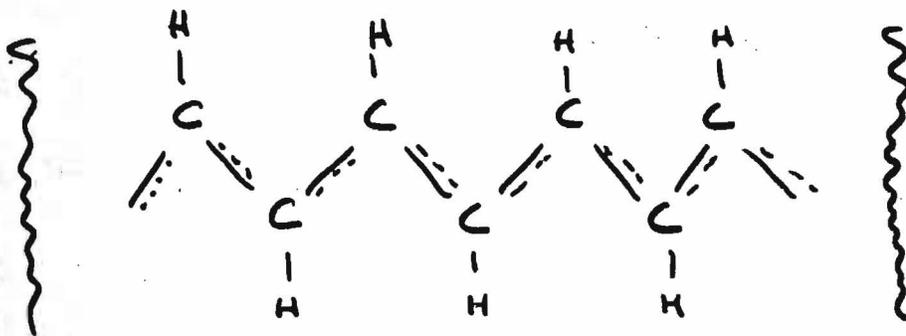
*Supported in part by the ONR.

EI 14 Band Structure of Polyacetylene, P. M. GRANT, IBM Research Laboratory, San Jose, CA--Using the extended Huckel method, we have calculated the one-dimensional band structure of polyacetylene in both cis- and trans-isomerization. For reasonable values of alternating carbon-carbon bond lengths, we find both structures lead to medium band gap (~ 1.5 eV) semiconductors with fairly wide valence and conduction bands (~ 5 eV), consistent with reported optical properties and estimated mobilities. The band gap in trans- $(\text{CH})_x$ appears at the Brillouin zone edge, while in cis- $(\text{CH})_x$ it is at zone center. Unlike some other semiconductors, such as polyethylene, the conduction band states in both forms are bound suggesting that donor as well as acceptor doping is possible. Variation of the density-of-states and effective masses with doping will be discussed on a rigid band interpretation of the movement of the Fermi level.

EI 15 Optical and Electrical Properties of Polydiacetylene Crystals. C. J. ECKHARDT, U. of Nebraska-Lincoln and R. R. CHANCE, Materials Research Center, Allied Chemical Corp.--Optical and photoconduction spectra for a number of polydiacetylene crystals will be compared and discussed. Without exception the photoconduction onsets are substantially blue-shifted (3000 cm^{-1} to 15000 cm^{-1}) with respect to optical absorption - a result which is consistent with an excitonic assignment for the lowest energy optical transition. Particular emphasis will be placed on a new

965 - IBM - 08

" sp^2 HYBRIDIZED TRANS- $(CH)_x$ SEGMENTS "



"GENERALIZED LCAO TIGHT-BINDING"

- BASIS SET: LC-BA-AO

$$\psi_{\vec{k}}(\vec{r}) = \sum_{p_j} c_{p_j} \sum_{\ell} e^{i\vec{k} \cdot \vec{R}_{\ell}} \varphi_p(\vec{r} - \vec{R}_{\ell} - \vec{r}_j)$$

- SECULAR EQUATION

$$\sum_{p_j} \left\{ \sum_{\ell} e^{i\vec{k} \cdot \vec{R}_{\ell}} \left[H_{\ell}(p_j', p_j) - E S_{\ell}(p_j', p_j) \right] \right\} c_{p_j} = 0$$

where:

$$S_{\ell}(p_j', p_j) = \int d^3r \varphi_{p_j'}^*(\vec{r} + \vec{R}_{\ell} - \vec{r}_j) \varphi_{p_j}(\vec{r} - \vec{r}_j)$$

- MWH FORM: USE MWH HAMILTONIAN
IN TERMS OF $S_{\ell}(p_j', p_j)$

"THE MULLIKEN-WOLFSBERG-HELMHOLTZ HAMILTONIAN"

- Let $\mathcal{O} = H$ in the Mulliken Theorem, then

$$H_{\mu\nu} = k \frac{S_{\mu\nu}}{2} [H_{\mu\mu} + H_{\nu\nu}]$$

- $k = 1.75$ as determined empirically

- CUSACH'S FORM:

- Accounts for observation that $T_{\mu\nu} \sim S_{\mu\nu}^2$

$$H_{\mu\nu} = (2 - |S_{\mu\nu}|) \frac{S_{\mu\nu}}{2} [H_{\mu\mu} + H_{\nu\nu}]$$

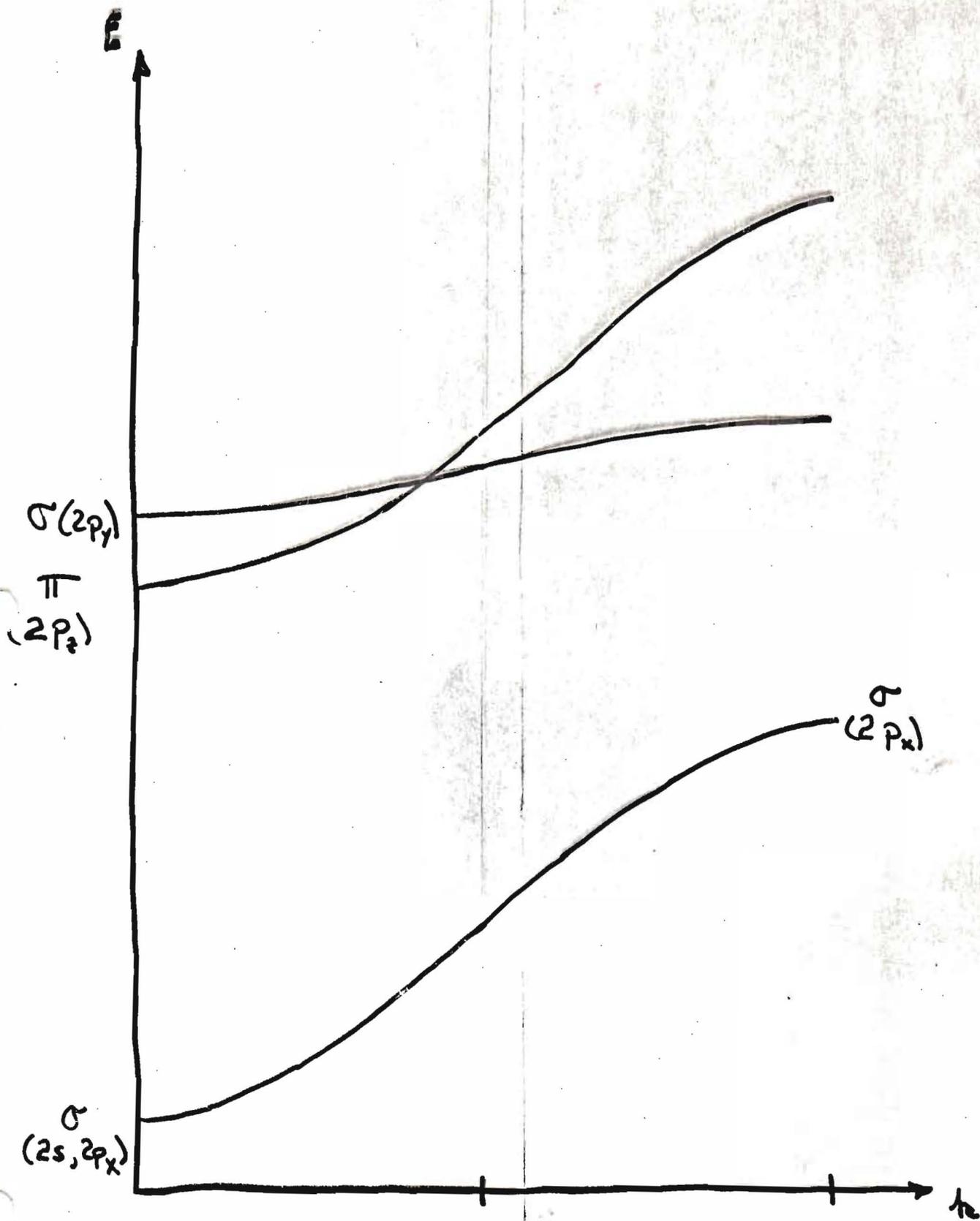
- PROGRAM

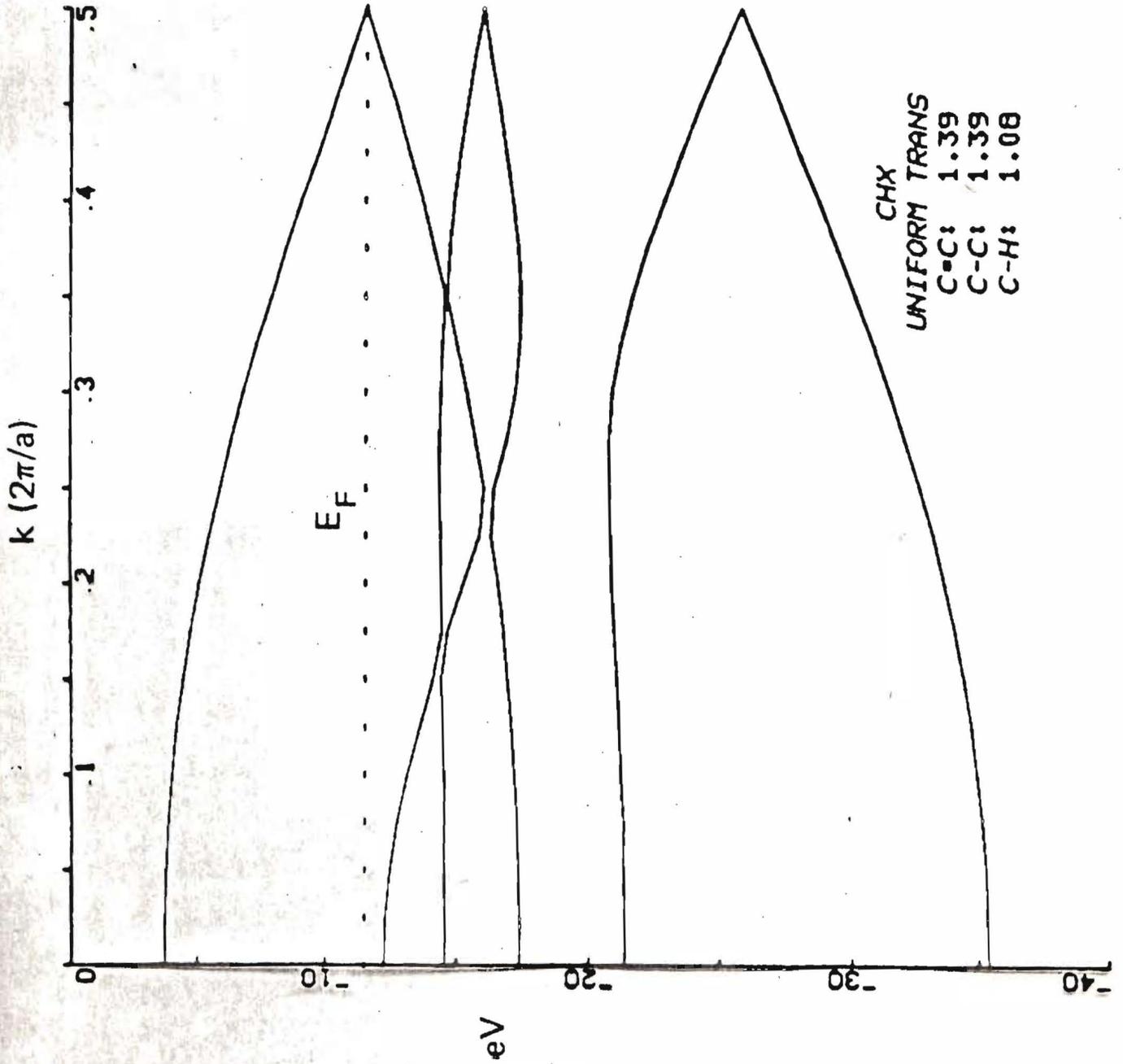
- Approximate $H_{\mu\mu}$ by appropriate calculated or measured ionization potentials
- Compute $S_{\mu\nu}$ in an appropriate one-electron basis like Slater fns or gaussians
- Diagonalize secular matrix

" CALCULATIONAL DETAILS "

- ATOMIC BASIS: Carbon sp^3 configuration
Multiple Slater Type Orbitals calculated
using Bagus - McLean - Yoshimine - Liu
SCF programs
- SECULAR MATRIX: Trans: 10 x 10
 Cis: 20 x 20
- OVERLAPS CALCULATED FROM CENTRAL CELL TO
NEAREST NEIGHBORS
- BOND LENGTHS CHOSEN TO RANGE BETWEEN
UNIFORM AND EXTREME ALTERNATION

" A GUESS AT TRANS- (CH)₂ BANDS "

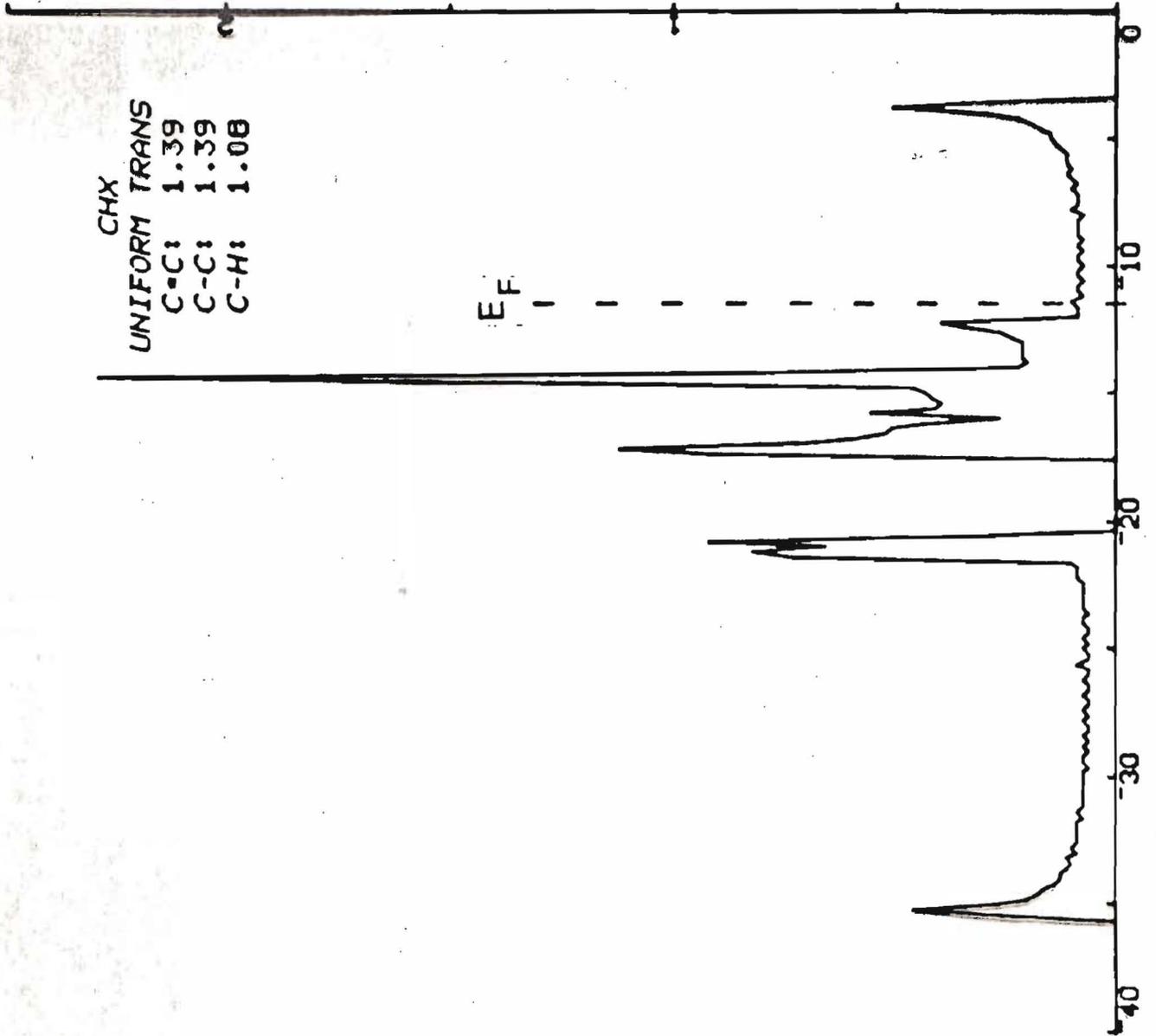


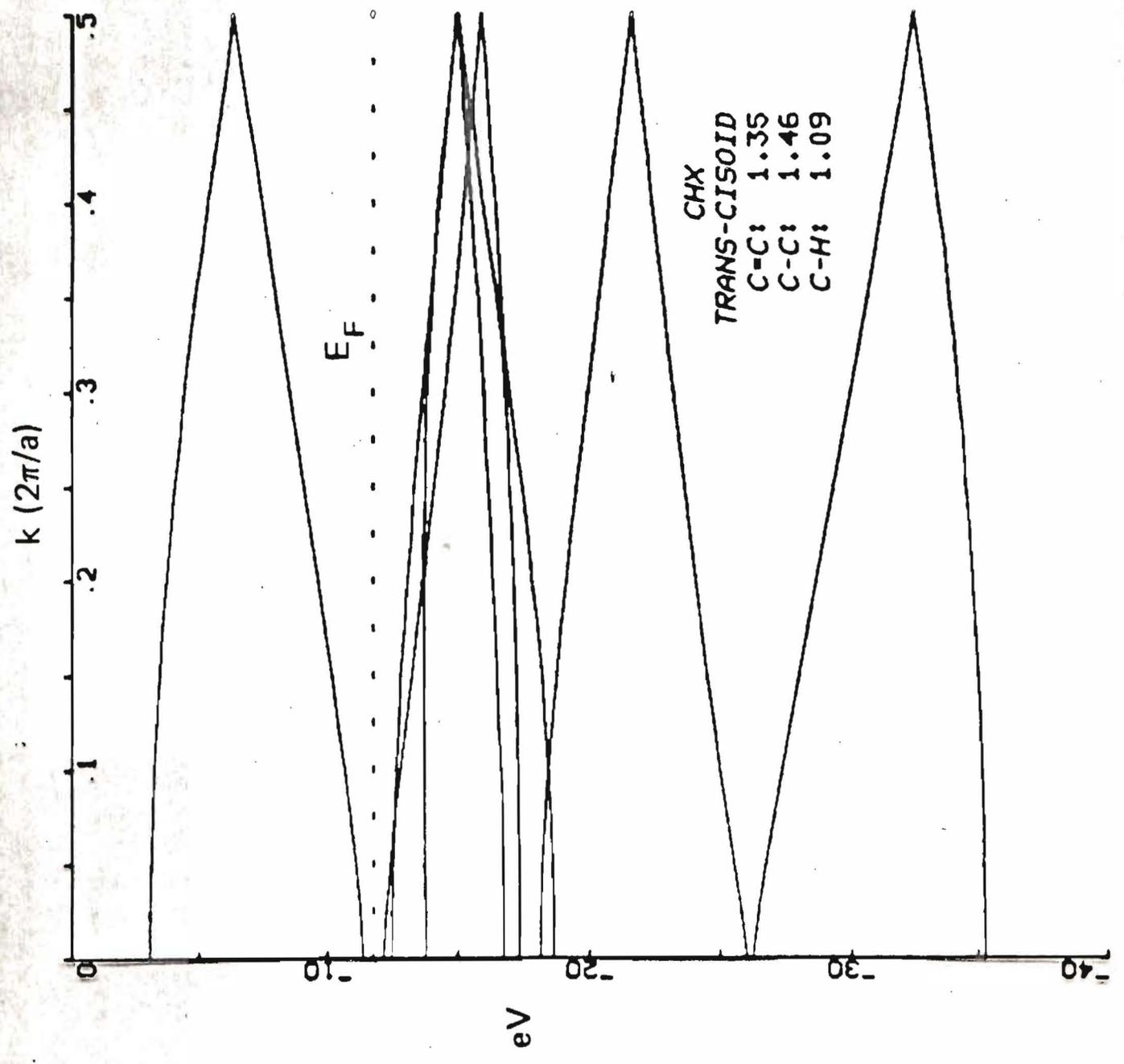


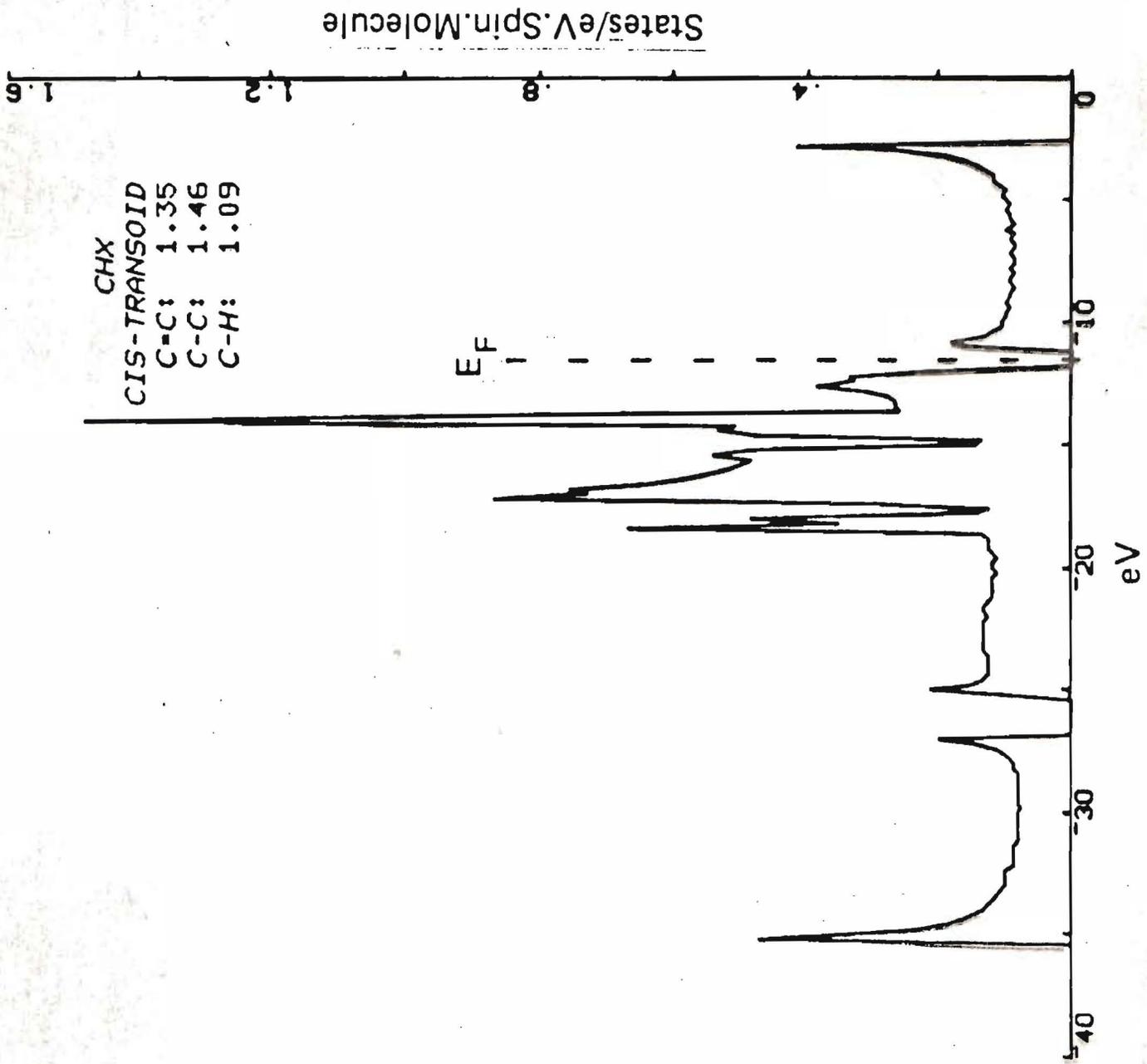
CHX
UNIFORM TRANS
C-C: 1.39
C-C: 1.39
C-H: 1.08

CHX
UNIFORM TRANS
C-C: 1.39
C-C: 1.39
C-H: 1.00

States/eV.Spin.Molecule







E_F

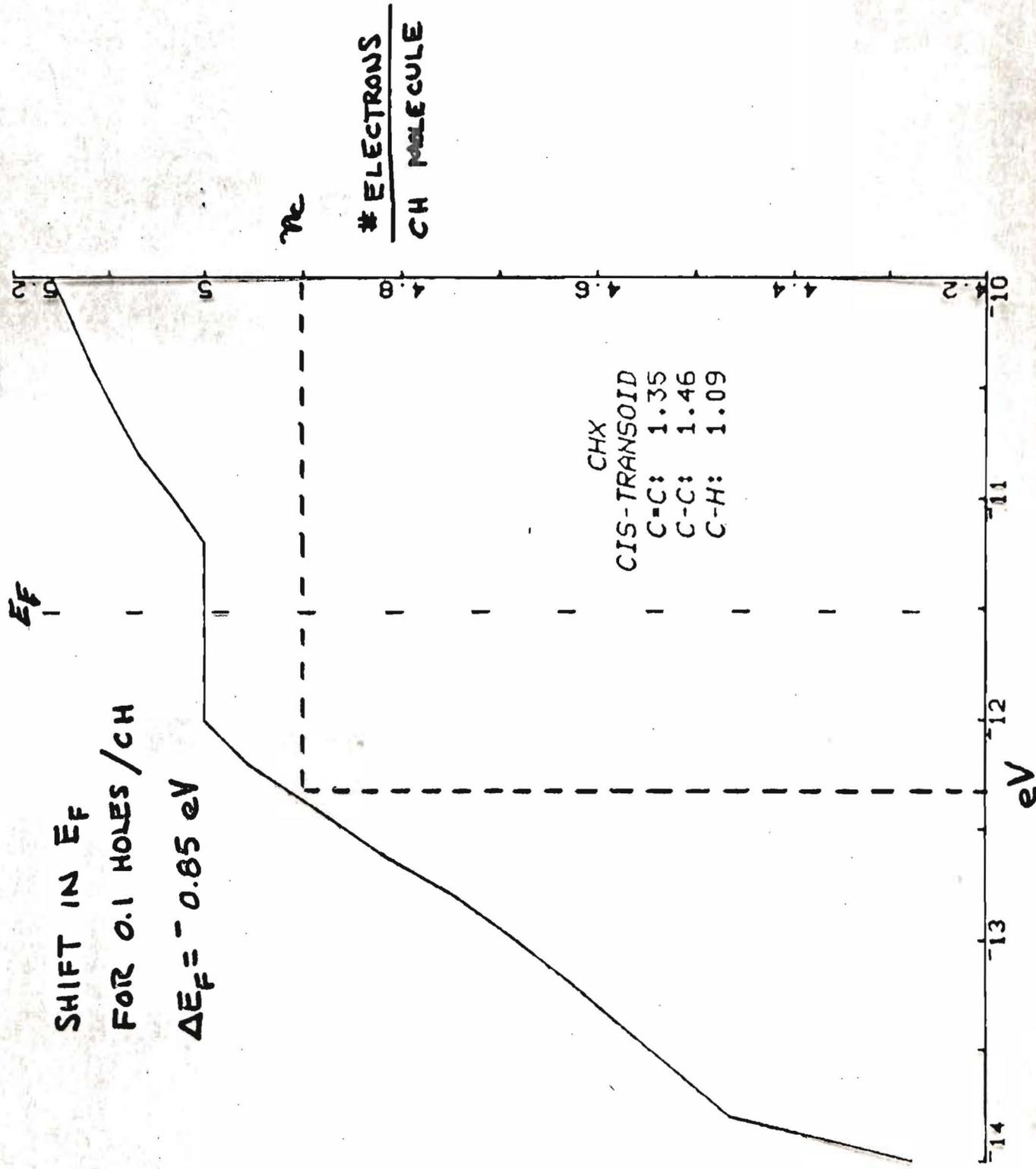
n_c

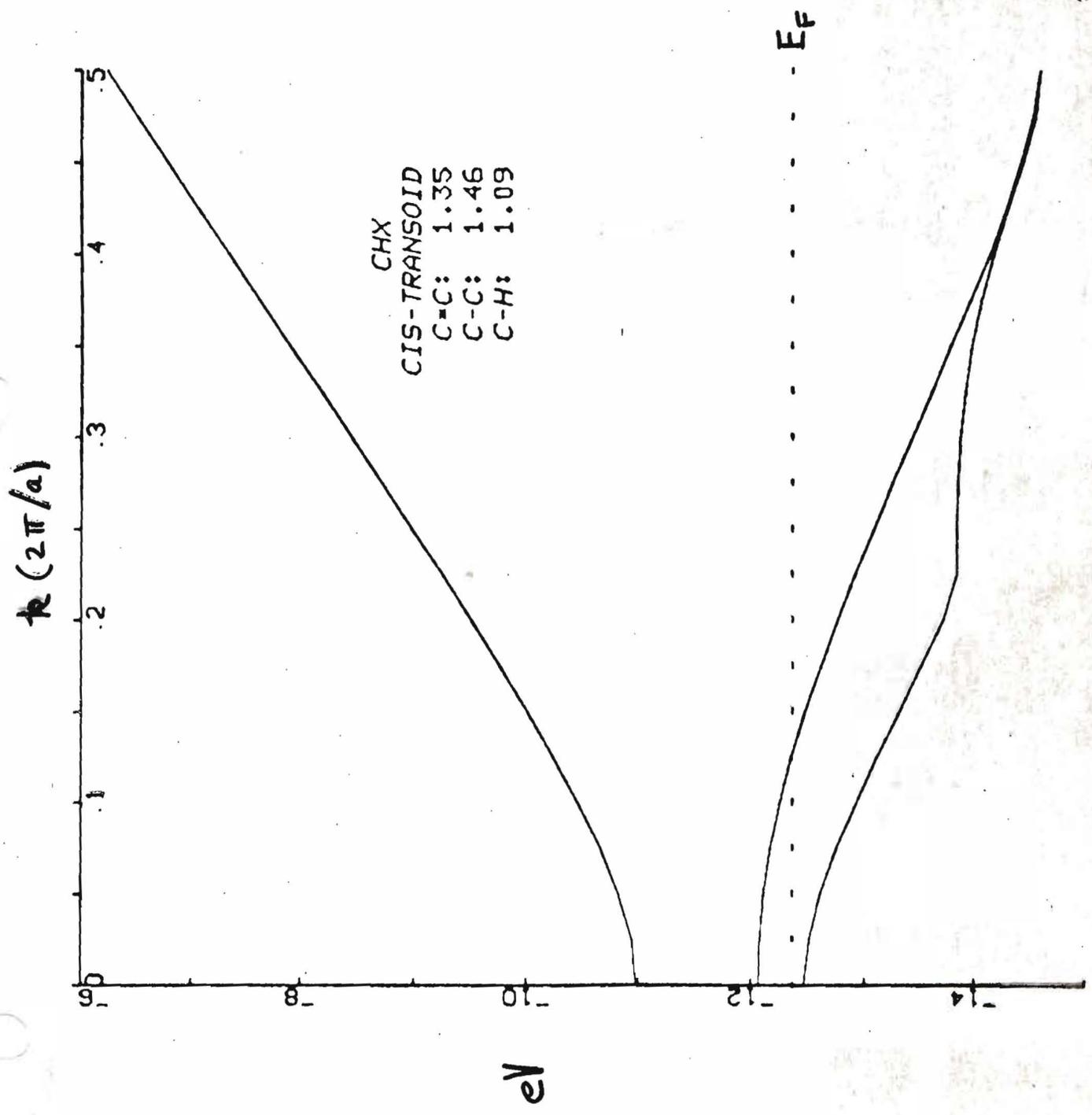
ELECTRONS
CH MOLECULE

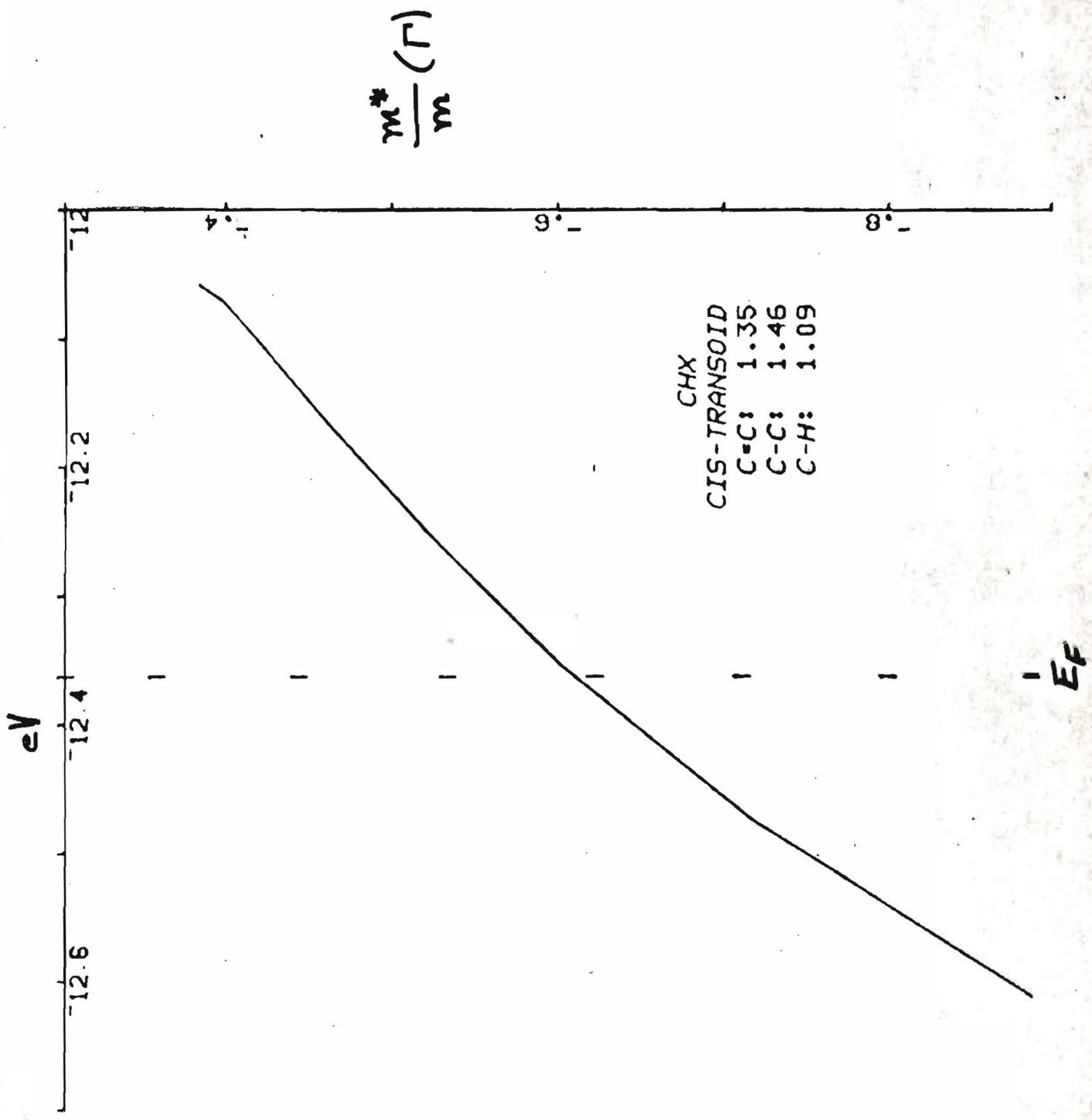
$$n_c(E) = \int_{-\infty}^E N(E') dE'$$

CHX
CIS-TRANSOID
C=C: 1.35
C-C: 1.46
C-H: 1.09









" AT THE END OF THE DAY ... "

- From an m^* point of view, it makes little difference if the host is cis or trans
- However, trans may offer more possibility for inter-valley particle-particle scattering thus resulting in lower ρ_{DC} than cis
- Both cis and trans have bound conduction band states, thus donor-doping is in principle possible, unlike polyethylene.