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On the Excess Electron and Hole Band Structures and Carrier Mobility in Naphthalene, Anthracene, and Several Polyphenyls

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The excess electron and hole band structures of naphthalene, anthracene, and several polyphenyls have been calculated in the tight binding approximation. In addition the anisotropy and the pressure dependence of the mobility tensor has been calculated in the constant-free-time and the constant-free-path approximations. The molecular wavefunctions were represented in the LCAO approximation using Hückel coefficients with the carbon atomic orbitals represented by the best available Hartree–Fock SCF carbon $2p$ ground-state function involving a linear combination of four Slater-type functions. By this choice of atomic orbitals, we hope to account properly for the behavior of the wavefunction at the large internuclear distances relevant to this problem. All of the above compounds are characterized by a crystal structure containing two molecules per unit cell. There are, therefore, two bands for both the electron and the hole cases. The bandwidths are calculated to be of the order of 0.1 eV. In the $\mathbf{a}^{-1}$ and $\mathbf{b}^{-1}$ directions, the symmetric and antisymmetric bands are degenerate at the zone edge. The electron bands are appreciably split in the $\mathbf{c}^{-1}$ direction.

Although there is no attempt to make absolute calculations of the mobility, the experimental data seem to be in adequate agreement with the scattering models considered. Inferences can be drawn which suggest that further understanding of the mobility will arise from a detailed investigation of the interaction of the charge carriers and the intermolecular and intramolecular vibrations.

I. INTRODUCTION

INTEREST in the electronic properties of organic molecular solids has steadily increased in the past decade. The major lines of investigation have fairly clear origins. For example, studies of the temperature dependence of the conductivity of aromatic and polymeric solids have been stimulated in part by the suggestion of Szent-Györgi[1] that macromolecules may play a role in electron transfer reactions of biological importance. Similarly, studies of the spin resonance spectra, conductivity, and related properties of charge-transfer complexes[2] owe much to Mulliken's theory of charge-transfer spectra[3] and to the observation that charge-transfer complexes may form in biological systems.[4] Finally, stimulated by the recent successes of solid state theory, important investigations of energy transfer, photoconductance, exciton spectra, etc., in molecular crystals have been made.[5] Despite great experimental difficulty, the following has been learned:

(a) The energy gap for conductivity in molecular aromatic crystals is quite large, typical values being of the order of 1 to 3 eV. The magnitude of the energy gap depends on the size of the aromatic molecules, the pressure, and the spectroscopic ground state.[6]

(b) Photoconductivity may be induced at a threshold energy much less than the ionization energy of the organic molecule, even when corrections for crystal polarization are made.[7] One possible interpretation of the observed facts is that the free carrier is generated by interaction between two excitons.[8] Recent experimental work by Silver confirms this mechanism for the bulk generation of carriers.[9] Generation of carriers at the surface of a crystal may occur by a different mechanism.

(c) It is generally true that charge-transfer complexes have much higher electrical conductivity than ordinary molecular solids.[6]

(d) Evidence is accumulating that triplet excitons can migrate more freely than heretofore supposed and energy transfer via triplet excitons has been conclusively demonstrated.[10]

(e) The best available evidence concerning electron and hole mobilities gives the order of magnitude of the mobility (in anthracene) as 1 cm^2 sec^{-1} V^{-1} at room temperature, and also indicates that the temperature dependence of the mobility is of the form T^{-n}, with $1<n<2$.[11]

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[1] A. Szent-Györgi, Science **93**, 609 (1941).

[2] See, for example, G. E. Blomgren and J. Kommandeur, J. Chem. Phys. **35**, 1636 (1961).

[3] R. S. Mulliken, J. Am. Chem. Soc. **74**, 811 (1952).

[4] See, for example, S. P. McGlynn, Radiation Res., Suppl. **2**, 300 (1960).

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[7] C. G. B. Garrett, Radiation Res., Suppl. **2**, 340 (1960).

[8] S. Choi and S. A. Rice, Phys. Rev. Letters **8**, 410 (1962); J. Chem. Phys. **38**, 366 (1963).

[9] M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, Phys. Rev. Letters **10**, 12 (1963).

[10] (a) R. W. Brandon, R. E. Gerkin, and C. A. Hutchison, Jr., J. Chem. Phys. **37**, 447 (1962); (b) G. C. Nieman and G. W. Robinson, *ibid.*, p. 2150.

[11] (a) R. G. Kepler, Phys. Rev. **119**, 1226 (1960); (b) R. G. Kepler in *Organic Semiconductors Conference*, edited by J. J. Brophy and J. W. Buttrey (The Macmillan Company, New York, 1962), p. 1.

Theoretical interpretations of the experimental facts cited have been sparse. Concerning Item (a), Evans and Gergely,[12] using a molecular orbital (MO) calculation, estimated the energy gap in polypeptides to be about 3 eV. However, their treatment of the electron delocalization via intermolecular hydrogen bonding is open to criticism, as it is well known that the MO approach breaks down for distances larger than about one and one-half times the intramolecular separation. These calculations should be made in the tight binding approximation, as is used in the present paper. Other attempts to discuss the dark conductivity of molecular solids have used very crude models and are not, in our opinion, satisfactory.[13] The only detailed quantum-mechanical calculations concerned with Item (b) are due to Choi and Rice who demonstrated that the two exciton mechanism cited was consistent with all available data.[8] Indeed, the recent experiments of Silver[9] provide quantitative verification of the Choi–Rice theory. Theoretical work connected with (c) and (d) has been primarily concerned with interpretation of electron spin resonance spectra. Finally, the interpretation of Item (e) has been attempted by LeBlanc.[14]

It is clear that a consistent interpretation of Items (a) to (e) would require a complete band-structure calculation, including the consideration of exciton states and varying lattice states. It is the purpose of this paper to take a first step in this direction by considering the band structure appropriate to an excess electron and to a hole in several organic molecular crystals. Only from a consistent discussion of the electronic band structure can all the relationships between Items (a) to (e) be revealed.

II. GENERAL REMARKS

The method of calculation adopted in this paper was introduced by LeBlanc[14] and also used recently by Thaxton *et al.*[15] While we confirm a number of LeBlanc's physical deductions, it can be seen in the following that the details of his calculation are open to criticism. LeBlanc assumed that the anthracene crystal, with two molecules per unit cell, could be related to a hypothetical crystal with one molecule per unit cell. This, however, is not possible. Corresponding to the two molecules per unit cell, there are two bands (arising from the symmetric and antisymmetric combinations of molecular wavefunctions in a cell) for the electron and two for the hole, whereas in the LeBlanc treatment there is only one for each. These two bands have interesting properties and are discussed in detail later.

The calculation of the excess electron or hole band energies requires knowledge of the detailed behavior of the molecular wavefunctions at large distances. To obtain numerical results, LeBlanc used 3.08 Å^{-1} as the value of the orbital exponent α in a Slater-type wavefunction for the carbon $2p$ atomic orbitals from which the molecular wavefunctions are constructed. We shall show that this value seriously underestimates the magnitude of the tails of the wavefunctions, and thus the use of a single Slater orbital is inappropriate. Clearly, the effective nuclear charge acting on an electron in a neutral atom or molecule decreases toward unity with increasing distance. The question of a proper representation of atomic and molecular wavefunctions at large distances is, in fact, not new. In 1931 Slater and Kirkwood[16] showed, in a classic calculation of the polarizability of the helium atom, that considerable improvement in quantities dependent on the tail region of the wavefunction can be achieved by using Slater-type wavefunctions with the effective nuclear charge $Z=1.0$ and the effective quantum number $n=0.745$ (instead of the values $Z=1.69$ and $n=1$ obtained from the simple variational treatment). The discrepancies between the more recent theoretical calculations of the quadrupole moments of simple polyatomic molecules[17] and the meager experimental data[18] are probably mainly due to the approximate representation of the molecular orbitals by linear combinations of Slater atomic orbitals (one on each atom), thereby seriously underestimating the charge distribution at large distances. A knowledge of the behavior of molecular wavefunctions at large R is also of great importance in current theoretical and experimental problems among which are the treatment of triplet excitation migration,[10] and the calculation of the Mulliken-type intermolecular charge-transfer interactions.[3] Clearly, the use of SCF atomic wavefunctions

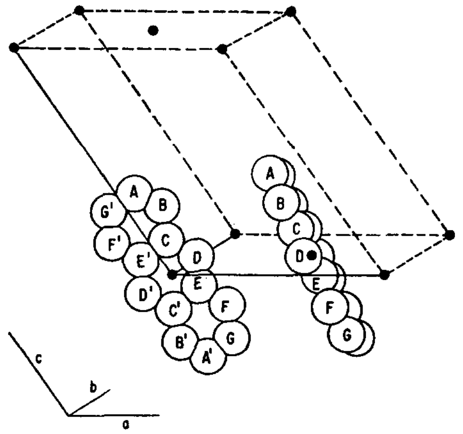

FIG. 1. Schematic representation of the unit cell showing the approximate orientation of the two molecules in the unit cell.

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[12] M. G. Evans and J. Gergely, Biochem. Biophys. Acta 3, 188 (1949).

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[14] O. H. LeBlanc, Jr., J. Chem. Phys. 35, 1275 (1960).

[15] G. D. Thaxton, R. C. Jarnagin, and M. Silver, J. Phys. Chem. 66, 2461 (1962).

[16] J. C. Slater and J. G. Kirkwood, Phys. Rev. 37, 682 (1931).

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[18] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1033.

for the construction of the molecular orbitals in the LCAO scheme should lead to much more accurate predictions. By the choice of these SCF atomic orbitals we hope to account properly for the behavior of the molecular wavefunctions at the large intermolecular distances relevant to the problem considered in this paper.

We find that the excess electron and hole bandwidths are very sensitive to the form of the wavefunctions and our calculations lead to bands about five times wider than found by LeBlanc. From the band structure thus obtained the mobility tensor is derived using primitive scattering models. We use these results to crudely account for electron and hole mobilities in aromatic crystals.

III. METHOD OF CALCULATION

All of the compounds discussed in this paper have crystal structures[19] described by the symmetry $C_{2h}{}^5 \equiv P2_1/a$. This structure has a monoclinic unit cell containing two molecules, one at the corner and the other in the center of the *ab* face. A schematic drawing of the unit cell is displayed in Fig. 1. Because there are two molecules per unit cells, we expect the electronic bands to have two branches corresponding to the symmetric and antisymmetric combinations of the basic molecular wavefunctions within the unit cell. We assume in the following that the concentration of excess electrons or holes is very small so that a one-particle treatment may be used. This condition is satisfied in all experiments conducted to date. Inasmuch as the binding energy of the molecular crystal is very small relative to the excitation energies of the various excited electronic states of the molecule (and crystal), the tight binding approximation may be employed. In this method one-electron crystal wavefunctions (unnormalized) are constructed from linear combinations of one electron molecular wavefunctions. The possible linear combinations, adapted for the translational symmetry of the crystal, are

$$\Psi_{\pm}(\mathbf{k}) = \sum_{l=0}^{N-1} \exp(i\mathbf{k}\cdot\mathbf{r}_l)[\phi(\mathbf{r}-\mathbf{r}_l) \pm C\,\theta(\mathbf{r}-\mathbf{r}_l-\boldsymbol{\beta})], \quad (1)$$

where the index l labels the unit cells and $0 \leq l \leq N$, N is the number of unit cells (one-half the number of molecules), the vector $\mathbf{r}_l$ locates the corner of the unit cell, $\boldsymbol{\beta}$ is the vector from the corner to the center of the *ab* face and ϕ, θ are the wavefunctions of molecule at the corner and the center of the unit cell, respectively. The constant C is a phase factor. It is clear that ϕ and θ are identical except for orientation in space. $E_{\pm}(\mathbf{k})$ is a double valued function corresponding to the two bands mentioned above. This behavior is to be expected since the two molecules of the unit cell are distinguishable (by virtue of orientation).

The phase factor C may be obtained from the condition that $\Psi_+(\mathbf{k})$ and $\Psi_-(\mathbf{k})$ be chosen to diagonalize the Hamiltonian. The general method of obtaining symmetry-adapted wavefunctions can be found in standard group theoretical textbooks.[20] It is found that $C = \exp(i\mathbf{k}\cdot\boldsymbol{\beta})$, whereupon Eq. (1) becomes

$$\Psi_{\pm}(\mathbf{k}) = \sum_{l=0}^{2N-1} (\pm 1)^l \exp(i\mathbf{k}\cdot\mathbf{r}_l)\phi(\mathbf{r}-\mathbf{r}_l), \quad (2)$$

where the index l labels the molecules which are now numbered so that the molecule at the corner of the cell has an even index while the one at the center of the cell has an odd index. Such a notation is less cumbersome than the customary notation where a double index notation is used to designate the unit cell and the molecule in the unit cell. Thus, in Eq. (2) the vector $\mathbf{r}_l$ is the vector to the center of each molecule, and one needs to recall that $\phi(\mathbf{r}-\mathbf{r}_l)$ has a different orientation in space depending on whether l is even or odd. LeBlanc and Thaxton *et al.* used only the symmetric function Ψ_+ in their calculations.

The Hamiltonian appropriate to an excess electron (or hole) has the form

$$H = (-\hbar^2/2m)\nabla^2 + V(\mathbf{r}), \quad (3)$$

where $V(\mathbf{r})$, which determines the crystal field, will be approximated by

$$V(\mathbf{r}) = \sum_n V_n(\mathbf{r}-\mathbf{r}_n) \quad (4)$$

with V_n the Hartree potential of an isolated neutral molecule. For an isolated molecular ion the Hamiltonian is

$$H_l^0 = (-\hbar^2/2m)\nabla^2 + V_n, \quad (5)$$

from which it follows that

$$e_0 = \int \phi^* H^0 \phi d\tau \quad (6)$$

is the energy of the isolated negative ion relative to infinite separation of the electron and the neutral molecule. The energy is a double valued function of $\mathbf{k}$ and is calculated from

$$E_+(\mathbf{k}) = \int \Psi^*_+ H \Psi_+ d\tau \Big/ \int \Psi^*_+ \Psi_+ d\tau,$$

$$E_-(\mathbf{k}) = \int \Psi^*_- H \Psi_- d\tau \Big/ \int \Psi^*_- \Psi_- d\tau, \quad (7)$$

after simplification by the use of several systematic approximations. With the neglect of three-center intermolecular integrals and overlap integrals multiplied by e_n or e_l, the substitution of Eqs. (3), (4), (5) and

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[19] A. I. Kitaĭgorodskiĭ, *Organic Chemical Crystallography* (Consultants Bureau, New York, 1961).

[20] S. L. Altman in *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1963), Vol. 2, p. 143.

(6) into Eq. (7) leads to

$$E_{\pm}(\mathbf{k})=e_0+\sum_n{}'e_n+\sum_l(\pm1)^l\cos(\mathbf{k}\cdot\mathbf{r}_l)e_l, \quad (8)$$

where the sums are taken over all molecules except the one with center located at the origin. Note that we neglect only those three-center integrals whose centers lie on three different molecules. All other three-center integrals are calculated and included in our treatment. The new symbols appearing in the above equation are defined as follows:

$$e_0=\int\phi^*H^0\phi d\tau, \quad (9)$$

$$e_n=\int\phi^*(\mathbf{r})V_n(\mathbf{r}-\mathbf{r}_n)\phi(\mathbf{r})d\tau, \quad (10)$$

$$e_l=\int\phi^*(\mathbf{r}-\mathbf{r}_l)V_l(\mathbf{r}-\mathbf{r}_l)\phi(\mathbf{r})d\tau. \quad (11)$$

In order to discuss the **k** variation of the energy bands, it is only necessary to examine the last term in Eq. (8):

$$E_{\pm}'(\mathbf{k})\equiv E_{\pm}(\mathbf{k})-e_0-\sum_n{}'e_n=\sum_l(\pm1)^l\cos(\mathbf{r}\cdot\mathbf{k}_l)e_l. \quad (12)$$

We have calculated all the integrals among the molecules on the corner and side centers of the unit cell. This is equivalent to the calculation of the integrals between the molecule in the position numbered 1 in Fig. 2 and the molecules in Positions 2 through 13. Because of its location, we have also included Molecule 14 in the calculation. Neglecting the interactions with other molecules (the nearest neglected molecule has no atoms closer than 7.5 Å) the energy dependence on **k** is

$$\begin{aligned}E_{\pm}'(\mathbf{k})=&2E_2\cos(\mathbf{k}\cdot\mathbf{c})+2E_3\cos(\mathbf{k}\cdot\mathbf{b})\\&+2E_4[\cos\mathbf{k}\cdot(\mathbf{b}+\mathbf{c})+\cos\mathbf{k}\cdot(\mathbf{b}-\mathbf{c})]\\&+2E_5\cos(\mathbf{k}\cdot\mathbf{a})+2E_6\cos\mathbf{k}\cdot(\mathbf{c}+\mathbf{a})\\&+2E_7[\cos\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})+\cos\mathbf{k}\cdot(\mathbf{a}-\mathbf{b})]\\&+2E_8[\cos\mathbf{k}\cdot(\mathbf{a}+\mathbf{b}+\mathbf{c})+\cos\mathbf{k}\cdot(\mathbf{a}-\mathbf{b}+\mathbf{c})]\\&\pm2E_9[\cos\mathbf{k}\cdot\tfrac{1}{2}(\mathbf{a}+\mathbf{b})+\cos\mathbf{k}\cdot\tfrac{1}{2}(\mathbf{a}-\mathbf{b})]\\&\pm2E_{10}[\cos\mathbf{k}\cdot[\tfrac{1}{2}(\mathbf{a}+\mathbf{b})+\mathbf{c}]+\cos\mathbf{k}\cdot[\tfrac{1}{2}(\mathbf{a}-\mathbf{b})+\mathbf{c}]\}\\&\pm2E_{11}\{\cos\mathbf{k}\cdot[\tfrac{1}{2}(\mathbf{b}-\mathbf{a})+\mathbf{c}]+\cos\mathbf{k}\cdot[\mathbf{c}-\tfrac{1}{2}(\mathbf{a}+\mathbf{b})]\}\\&+2E_{12}[\cos\mathbf{k}\cdot(\mathbf{c}-\mathbf{a})\\&+2E_{13}[\cos\mathbf{k}\cdot(\mathbf{b}-\mathbf{a}+\mathbf{c})+\cos\mathbf{k}\cdot(\mathbf{c}-\mathbf{a}-\mathbf{b})]\\&\pm2E_{14}[\cos\mathbf{k}\cdot\tfrac{1}{2}(\mathbf{a}+3\mathbf{b})+\cos\mathbf{k}\cdot\tfrac{1}{2}(\mathbf{a}-3\mathbf{b})], \quad (13)\end{aligned}$$

where the 13 E_i are the resonance integrals between Molecules 1 and i such as given by e_l in Eq. (11).

The band can be readily visualized if we consider now the special cases when **k** is parallel to a reciprocal lattice vector $\mathbf{a}^{-1}$, $\mathbf{b}^{-1}$, or $\mathbf{c}^{-1}$:

$$E_{\pm}'(\mathbf{k}\parallel\mathbf{a}^{-1})=A+B\cos(\mathbf{k}\cdot\mathbf{a})\pm C\cos(\mathbf{k}\cdot\mathbf{a}/2), \quad (14)$$

$$\begin{aligned}E_{\pm}'(\mathbf{k}\parallel\mathbf{b}^{-1})=&D+E\cos(\mathbf{k}\cdot\mathbf{b})\pm F\cos(\mathbf{k}\cdot\mathbf{b}/2)\\&\pm E_{14}\cos(\mathbf{k}\cdot3\mathbf{b}/2), \quad (15)\end{aligned}$$

$$\begin{aligned}E_{+}'(\mathbf{k}\parallel\mathbf{c}^{-1})&=G+H\cos(\mathbf{k}\cdot\mathbf{c}),\\E_{-}'(\mathbf{k}\parallel\mathbf{c}^{-1})&=I+J\cos(\mathbf{k}\cdot\mathbf{c}), \quad (16)\end{aligned}$$

where we have defined A through J by the relations

$$\begin{aligned}A&=2(E_2+E_3+2E_4),\\B&=2(E_5+E_6+2E_7+2E_8+E_{12}+2E_{13}),\\C&=4(E_9+E_{10}+E_{11}+E_{14}),\\D&=2(E_2+E_5+E_6+E_{12}),\\E&=2(E_3+2E_4+2E_7+2E_8+2E_{13}),\\F&=4(E_9+E_{10}+E_{11}),\\G&=2(E_3+E_5+2E_7+2E_9+2E_{14}),\\H&=2[E_2+2E_4+E_6+2E_8+E_{12}+2E_{13}+2(E_{10}+E_{11})],\\I&=2(E_3+E_5+2E_7-2E_9-2E_{14}),\\J&=2[E_2+2E_4+E_6+2E_8+E_{12}+2E_{13}-2(E_{10}+E_{11})]. \quad (17)\end{aligned}$$

It might seem, from Eqs. (14) and (15), that $E(\mathbf{k})$ has a periodicity of $4\pi\mathbf{a}^{-1}$ and $4\pi\mathbf{b}^{-1}$. It should be noted, however, that this is not so by virtue of the relations

$$\begin{aligned}\Psi_+(\mathbf{k}+2\pi\mathbf{a}^{-1})&=\Psi_-(\mathbf{k}),\\\Psi_-(\mathbf{k}+2\pi\mathbf{a}^{-1})&=\Psi_+(\mathbf{k}), \quad (18)\\\Psi_+(\mathbf{k}+2\pi\mathbf{b}^{-1})&=\Psi_-(\mathbf{k}),\\\Psi_-(\mathbf{k}+2\pi\mathbf{b}^{-1})&=\Psi_+(\mathbf{k}), \quad (19)\end{aligned}$$

and when $\mathbf{k}=\pi\mathbf{a}^{-1}$ or $\mathbf{k}=\pi\mathbf{b}^{-1}$, from Eq. (1) we see

$$\Psi_+(\mathbf{k})=\sum_{l=0}^{N-1}\exp(il\pi)[\phi_l+\exp(i\pi/2)\theta_l]=\Psi_-^*(\mathbf{k}), \quad (20)$$

which proves Ψ_+ and Ψ_- have the same energy at $\pi\mathbf{a}^{-1}$ and $\pi\mathbf{b}^{-1}$. Thus in going from the first to the second Brillouin zone Ψ_+ and Ψ_- cross and interchange roles in the $\mathbf{a}^{-1}$ and $\mathbf{b}^{-1}$ directions, and there is therefore the expected periodicity of $2\pi\mathbf{a}^{-1}$ and $2\pi\mathbf{b}^{-1}$. The

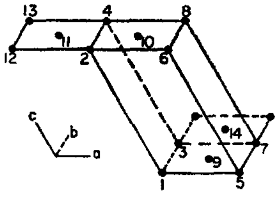

FIG. 2. Schematic representation of the unit cell showing the numbering of the molecules used in this paper.

second half of the band calculated by LeBlanc[14] is the second band mirrored through an axis at $2\pi\mathbf{a}^{-1}$ or $2\pi\mathbf{b}^{-1}$.

IV. NUMERICAL CALCULATIONS

The first step in making numerical calculations from the equations of Sec. II is the selection of a suitable molecular wavefunction for the molecular ion. The simplest approximation to the molecular wavefunction would place the extra electron in the first unoccupied molecular orbital of the neutral molecule and describe the electronic motion as if the interaction between electron and molecule caused no change in the orbital in question. Thus, Balk *et al.*[21] have shown that the properties of isolated negative aromatic ions can be understood if the orbital occupied by the excess electron is described by the Hückel coefficients characteristic of the first unoccupied orbital or the neutral molecule.

It is interesting to note that Hückel functions are not unreasonable approximations to self-consistent field functions with differential overlap neglected. The Balk approximation rests on two considerations:

(a) Pople[22a] proved that the Coulson and Rushbrooke theorem[22b] remains valid in the more general SCF scheme, i.e., the π electrons are uniformly distributed in the ground state and in singly excited states.

(b) Given the uniform charge distribution cited, it may be guessed that the addition of one electron will not grossly change the charge distribution of the original electrons. Certainly this will only be even approximately true if the π-electron system is large.

In the mononegative ion, excitations are then described in terms of promotion of the extra electron, the remaining system being considered to be the original molecule in the ground state or in an excited states. It should be noted that even if the suppositions made were exactly true, the neglect of exchange between the extra electron and the core electrons prevents the orbital described from becoming the one electron self-consistent field orbital.

It is clear that the Balk approximation will be best if the neutral core remains the same and only excitations of the extra electron are considered. Indeed, these are just the terms considered in our present calculation of $E(\mathbf{k})$. Before proceeding, however, it is necessary to remark that the Pariser–Parr or Pople theories of hydrocarbon spectra fail in the calculation of ionization energies although they are very successful in describing electronic spectra. Hoyland and Goodman[23] have traced the difficulties to three factors:

(a) The effect of π-electron ionization or capture on the framework of the molecule;

(b) The changes in π basis functions upon π-electron ionization or capture;

(c) Changes in the π-electron molecular orbitals through construction of a new Hartree–Fock Hamiltonian for the resulting ion and subsequent reminimization of the energy.

By combining the Pariser–Parr formulation of π electron theory[24] with Roothaan's self-consistent field theory and deformation of orbital assumptions, excellent agreement between computed and measured ionization potentials is obtained. The wavefunctions also differ from those characteristic of the Hoijtink approximation.

Because of the importance of the choice of the molecular wavefunctions, we have made calculations using both the Balk approximation and the wavefunctions computed by Hoyland and Goodman whenever possible (naphthalene and anthracene). In general, it is found that there is little difference between the results obtained from the two different wavefunctions (see Tables II through V). This fact supports the general conclusions drawn from the simpler wavefunctions used for all compounds considered in this paper.

At this point it is convenient to consider the approximations involved in obtaining numerical results from Eq. (12). The molecular orbitals of a positive or negative ion are approximated by a linear combination of neutral carbon $2p_z$ wavefunctions u_i

$$\phi_n = \sum_i C_{ni} u_i, \tag{21}$$

where the C_{ni} are Hückel coefficients without overlap or the coefficients given by Hoyland and Goodman.[23] As already mentioned, the use of single Slater orbitals characterized by a single orbital exponent is inappropriate. The Slater-type function has only one adjustable parameter and this is chosen to minimize the energy of the atom. Since the tail (large R) of the wavefunction makes only a small contribution to the energy of the atom, it is very poorly represented by the usual Slater function. The integrals of greatest interest in the present calculation involve atoms centered on different molecules, and it is the large R portion of the wavefunction which is of interest to us. One expects that the Hartree–Fock wavefunction would be better everywhere, and in particular better in the tail.

One possible method to obtain a reasonable approximation to the tail of the wavefunction is to try to fit a single Slater-type function to the atomic SCF functions, adjusting the orbital exponent to give the best fit at

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[21] P. Balk, S. De Bruijn, and G. J. Hoijtink, Recueil Trav. Chim. Pays Bas **76**, 860 (1957).

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[24] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953).

large distances. However, using the best available neutral carbon atom SCF $2p$ function we found that a good fit cannot be obtained in the region 1–4 Å using a wavefunction characterized by a single orbital exponent. Since the resonance and overlap integrals are very sensitive to the detailed form of the wavefunction, we used in our calculations the best available carbon atom wavefunction represented in the form of a linear combination of four Slater wavefunctions[25]

$$u_i(\mathbf{r})=(\mathbf{n}_i\cdot\mathbf{r})\sum_{i=1}^{4}a_i(\alpha_i^5/\pi)^{\frac{1}{2}}\exp(-\alpha_i r). \qquad (22)$$

Here $\mathbf{n}_i$ is the unit vector defining the direction of the $2p$ orbital. The coefficients a_i and orbital exponents α_i are those given by Clementi and Roothaan.[25]

The potential energy of the molecule is a linear combination of neutral-carbon-atom potentials. These are derived from classical electrostatic arguments in the spirit of the Hartree method by averaging over the four ($2s$, $2p_x$, $2p_y$, and $2p_z$) electrons. We thus approximate the potential energy of a neutral molecule by

$$V_n=\sum_i V_i, \qquad (23)$$

where V_i is the Goeppert-Mayer and Sklar[26] potential of Carbon Atom i.

Using Eq. (22) for u_i we obtain

$$V_i=-\frac{e^2}{r_i}\left(\sum_{k,l}\frac{a_l\alpha_l^{5/2}a_k\alpha_k^{5/2}}{\beta_{kl}^5}\right)^{-1}\sum_{k,l}\exp(-2\beta_{kl}r_i)$$
$$\times\frac{a_k\alpha_k^{\frac{5}{2}}a_l\alpha_l^{\frac{5}{2}}}{\beta_{kl}^5}[\tfrac{4}{3}(\beta_{kl}r_i)^3+4(\beta_{kl}r_i)^2+6(\beta_{kl}r_i)+4], \qquad (24)$$

where $\beta_{kl}=\frac{1}{2}(\alpha_k+\alpha_l)$.

On expanding the intermolecular integrals using Eqs. (22) and (23) one finds

$$e_l=\int\phi(\mathbf{r})V(\mathbf{r})\phi(\mathbf{r}-\mathbf{r}_l)d\tau$$
$$=\sum_{i,j,m}C_{\alpha i}C_{\beta j}\int u_i(\mathbf{r}-\mathbf{r}_i)V_m(\mathbf{r}-\mathbf{r}_m)u_j(\mathbf{r}-\mathbf{r}_l-\mathbf{r}_j)d\tau. \qquad (25)$$

LeBlanc and Thaxton *et al.* neglected those terms in the sum where i does not equal m. In other words, they only calculated two-center integrals and neglected not only those three-center integrals in which the centers are on three different molecules (in which case since all the interatomic distances are very large these are truly negligible terms) but also those terms in which the potential and one wavefunction are on the same molecule, while the other wavefunction is on a different molecule. Since the nearest interatomic distance is only 1.4 Å these terms are *not* small, and there are many of them. As can be seen from Table II these integrals change the energy by about 25%. Both the two and the three-center integrals were calculated numerically using an IBM 7090 computer. The two-center integrals we simplified by expanding in the form

$$-\pi^{-1}\frac{(\mathbf{n}_i\cdot\mathbf{R}_{ij})(\mathbf{n}_j\cdot\mathbf{R}_{ij})}{R_{ij}^2}S_{ij}$$
$$+2\pi^{-1}\left[(\mathbf{n}_i\cdot\mathbf{n}_j)-\frac{(\mathbf{n}_i\cdot\mathbf{R}_{ij})(\mathbf{n}_j\cdot\mathbf{R}_{ij})}{R_{ij}^2}\right]C_{ij}, \qquad (26)$$

where $\mathbf{n}_i$ and $\mathbf{n}_j$ are the unit vectors defining the direction of orbital u_i and u_j, $\mathbf{R}_{ij}$ is the vector from Atom i to Atom j, and

$$S_{ij}=\int r_ir_j\cos\gamma_i\cos\gamma_jV_i[\sum_l a_l\alpha_l^{5/2}\exp(-\alpha_lr_i)]$$
$$\times[\sum_m a_m\alpha_m^{5/2}\exp(-\alpha_mr_j)]d\tau,$$

$$C_{ij}=\int r_ir_j\sin\gamma_i\sin\gamma_jV_i[\sum_l a_l\alpha_l^{5/2}\exp(-\alpha_lr_i)]$$
$$\times[\sum_m a_m\alpha_m^{5/2}\exp(-\alpha_mr_j)]d\tau, \qquad (27)$$

where γ_i and γ_j are the angles $\mathbf{r}_i$ and $\mathbf{r}_j$ make with $\mathbf{R}_{ij}$. Both S_{ij} and C_{ij} are cylindrically symmetric and can therefore be reduced to a double integration. By a careful choice of coordinates, one of the integrations can be performed analytically leaving only a one dimensional integration. All integrals involving coordinates of atoms closer than 10 Å were included. However, none of the above simplifications were possible with the three-center integrals. These were performed by a three-dimensional Gaussian integration using 6000 points. Only those integrals in which the potential and wavefunction on the same molecule were on near-neighbor atoms were performed, and of them, only those where the distance between the two wavefunctions was less than 6.5 Å. Even with these limitations several hundred such integrals had to be performed for each compound. Such a program requires approximately 1 h of computing time on an IBM 7090. In contrast, all the two-center integrals for a compound are calculated in 1 min. It should be noted, however, for the case of atomic orbitals represented by a single Slater-type function, that the equations given by LeBlanc and also used by Thaxton *et al.* for S_{ij} and C_{ij} are incorrect. For this case Eq. (27) is reduced to the form

$$(1/\pi)S_{ij}(t)=(-e^2\alpha/2^7t^3)e^{-t}(1386+1386t+693t^2$$
$$-1596t^3+536t^4),$$
$$(1/2\pi)C_{ij}(t)=(-e^2\alpha/2^8t^3)e^{-t}(1386+1386t$$
$$-2120t^2+1072t^3), \qquad (28)$$

where $t=\alpha R_{ij}$.

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[25] E. Clementi and C. C. J. Roothaan, Phys. Rev. **127**, 1618 (1962).

[26] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

TABLE I. Crystal constants.

	a	b	c	β
Naphthalene[29a]	8.235 Å	6.003 Å	8.658 Å	122°55′
Anthracene[29b]	8.561 Å	6.036 Å	11.163 Å	124°42′
Biphenyl[29c]	$8.12_4\pm0.02$ Å	$5.63_5\pm0.01$ Å	$9.51_3\pm0.02$ Å	$95.1°\pm0.3°$
Terphenyl[29d]	8.08 Å	5.60 Å	13.59 Å	91°55′
Quaterphenyl[29e]	8.05 ± 0.02 Å	5.55 ± 0.02 Å	17.81 ± 0.05 Å	95.8° (approx.)
Terphenyl[29f] (Hertel and Römer)	8.14 Å	5.64 Å	14.10 Å	105°

When a standard approximation such as the Mulliken approximation,[27]

$$\phi_i\phi_j=\tfrac{1}{2}S_{ij}(\phi_i^2+\phi_j^2), \tag{29}$$

is used where

$$S_{ij}=\int\phi_i\phi_j d\tau; \tag{30}$$

or, if the Sklar approximation[28]

$$\phi_i\phi_j=S_{ij}\phi_F^2 \tag{31}$$

is employed, where ϕ_F is a function centered at a point F located midway between points i and j, poor numerical predictions of the three-center integrals are obtained. The approximations mentioned (Mulliken and Sklar) are useful only when the three centers are not far apart and when the potential is a *slowly* decreasing function of distance.

V. NUMERICAL RESULTS FOR BAND STRUCTURE CALCULATIONS

The crystal data for the aromatic compounds[29] used in our numerical calculations are listed in Table I. The experimental data are best for napthalene, anthracene, and biphenyl. The naphthalene and anthracene data are accurate to at least 0.02 Å as can be inferred from the reported standard deviation in the atomic coordinates. The available data for terphenyl and quaterphenyl are very poor, certainly no better than 0.4 Å. The claimed experimental accuracies are listed in Table I. However, as can be seen from the two sets of data given for terphenyl, the differences between the measurements of different investigators are great. We have used the first set of data including atomic coordinates given by Pickett.[29d]

In Table II we display the resonance integrals calculated between the molecule at Position 1, the corner of the unit cell, and the other 13 neighbor molecules (Fig. 2). We have thus included all integrals between molecules containing carbon atoms closer than 7.5 Å from each other. For naphthalene, anthracene, and biphenyl we give the results of calculations including the contribution of the three-center integrals comparing them with computations where only the two-center integrals were considered. Calculations were also performed using Hoyland and Goodman's coefficients[23] instead of Hückel coefficients[30] for the two-center integrals.

For a proper comparison of our results with those of LeBlanc and of Thaxton *et al.*, we also include the case where the carbon atom wavefunctions are characterized by a single Slater-type exponent, $\alpha=3.08$ Å^{-1}. The difference between these values and those of LeBlanc is due to the use of the corrected Eq. (28) and to the inclusion of all integrals between atoms from 5.0 to 7.5 Å apart, which they neglected. In Table III we present the intermolecular overlap integrals calculated using the SCF functions and also for a single Slater-type function with $\alpha=3.08$ Å^{-1}. For the case of anthracene we have also included the results for a single Slater-type function with $\alpha=3.072$ Å^{-1} to permit correction of the overlap integral calculated by Murrell[31] who included only those atom pairs 4.5 Å or less apart. These results demonstrate the effect of using the SCF wavefunction, thus accounting properly for the tail of the molecular wavefunctions. In Figs. 3 to 8 we have plotted the excess electron and hole band structure in the reciprocal crystal axis direction for naphthalene, anthracene and biphenyl, including the contribution of the three center integrals. We have not plotted the shapes of the bands for any of the other cases; however, these can be easily calculated using Eqs. (14), (15), (16), and (17) and the data given in Table II. In Table IV we display the values of the widths of the bands in the $\mathbf{a}^{-1}$, $\mathbf{b}^{-1}$, and $\mathbf{c}^{-1}$ directions. Whenever the bands in the $\mathbf{c}^{-1}$ direction are split we have also given the appropriate splitting.

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[29] (a) D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957); (b) V. C. Sinclair, J. M. Robertson, and A. M. Mathieson, *ibid.* **3**, 251 (1950); (c) A. Hargreaves and S. Hason Rizvi, *ibid.* **15**, 365 (1962); (d) L. W. Pickett, Proc. Roy. Soc. (London) **A142**, 333 (1933); (e) L. W. Pickett, J. Am. Chem. Soc. **58**, 2299 (1936); (f) E. Hertel and G. H. Romer, Z. Phys. Chem. **22**, 292 (1933).

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[31] J. N. Murrell, Mol. Phys. **4**, 205 (1961).

TABLE II. Intermolecular resonance integrals in units of 10^{-4} eV.[a]

	Two-center integrals only						
Molecule number	Naphthalene	Anthracene	Biphenyl	Terphenyl	Quaterphenyl	Naphthalene (H. and G. coefficients)	Anthracene (H. and G. coefficients)
				Hole			
2	−0.33	−0.30	−81.61	−46.10	−29.95	−0.31	−0.27
3	−96.46	−111.85	65.35	77.82	89.43	−96.90	−104.21
4	−1.76	−0.17	0.15	0.08	0.04	−1.75	−0.15
5	0.27	0.20	−0.51	−0.51	−0.41	0.27	0.02
6	8.22	−3.53	−2.11	0.00	0.00	8.12	−3.69
7	0.32	0.03	0.00	−0.01	−12.17	0.32	0.00
8	0.05	−0.03	−0.10	0.00	0.01	0.05	−0.03
9	29.26	−85.45	15.18	−2.85	12.17	27.39	−80.00
10	−33.51	29.89	26.44	0.01	1.06	−32.20	24.91
11	−0.02	0.01	−0.01	15.34	12.61	−0.02	0.01
12	0.00	0.00	0.00	−1.08	−0.55	0.00	0.00
13	0.00	0.00	0.00	−0.07	−0.03	0.00	0.00
14	0.04	0.01	0.00	0.00	0.00	0.04	0.01
				Electron			
2	−5.27	0.19	−3.65	4.07	5.53	−4.91	0.21
3	21.77	67.04	90.57	124.95	154.49	23.82	70.29
4	0.16	−0.03	0.00	0.03	0.03	0.20	−0.02
5	0.00	0.25	0.21	0.43	0.37	−0.02	0.23
6	1.92	−0.80	0.61	0.00	0.00	1.78	−0.54
7	−0.05	0.04	0.00	0.10	0.12	−0.05	0.02
8	−0.03	0.02	0.02	0.00	0.00	−0.03	0.01
9	−54.00	−115.56	−48.39	−68.73	−65.72	−55.19	−115.82
10	−3.44	2.25	−11.91	−0.05	−0.04	−2.66	1.20
11	−0.03	0.02	−0.07	−8.07	−8.35	−0.02	0.02
12	0.00	0.00	0.00	0.37	0.22	0.00	0.00
13	0.00	0.00	0.00	0.02	0.01	0.00	0.00
14	0.01	0.00	0.01	0.02	0.02	0.01	0.00

	Two- and three-center integrals			Two-center integrals only			
Molecule number	Naphthalene	Anthracene	Biphenyl	Naphthalene $\alpha=3.08$	Anthracene $\alpha=3.08$	Biphenyl $\alpha=3.08$	Terphenyl $\alpha=3.08$
				Hole			
2	−0.36	−0.47	−104.12	−0.07	0.07	−12.24	−7.01
3	−120.97	−132.44	78.01	−14.19	−20.71	10.08	13.92
4	−1.76	−0.17	0.20	−0.01	0.00	0.00	0.00
5	0.27	0.20	−0.51	0.00	0.00	0.00	0.00
6	11.18	−4.39	−2.72	0.20	−0.09	−0.03	0.00
7	0.32	0.03	0.00	0.00	0.00	0.00	0.00
8	0.05	−0.03	−0.10	0.00	0.00	0.00	0.00
9	39.30	−93.05	19.65	−0.24	−18.35	0.59	−1.51
10	−42.50	36.61	32.88	−3.90	4.15	2.55	0.00
11	−0.02	0.01	−0.01	0.00	0.00	0.00	1.59
12	0.00	0.00	0.00	0.00	0.00	0.00	−0.01
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.04	0.01	0.00	0.00	0.00	0.00	0.00
				Electron			
2	−5.60	0.15	−1.23	−1.20	0.38	−0.83	0.73
3	22.77	71.61	100.49	4.84	15.63	15.32	22.58
4	0.16	−0.03	0.00	0.00	0.00	0.00	0.00
5	0.00	0.25	0.21	0.00	0.00	0.00	0.00
6	3.51	−0.74	0.87	0.06	−0.03	0.01	0.00
7	−0.05	0.04	0.00	0.00	0.00	0.00	0.00
8	−0.03	0.02	0.02	0.00	0.00	0.00	0.00
9	−52.46	−124.79	−59.11	−13.46	−24.82	−11.40	−16.77
10	−3.37	2.48	−12.99	−0.68	0.67	−1.42	0.00
11	−0.03	0.02	−0.07	0.00	0.00	0.00	−0.99
12	0.00	0.00	0.00	0.00	0.00	0.00	0.01
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.01	0.00	0.00	0.00	0.00	0.00	0.00

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[a] Unless otherwise noted the entries in these tables refer to the case where the atomic wavefunction is represented as a sum of the four Slater functions and the molecular wavefunction is constructed of Hückel orbitals. When the Hoyland and Goodman wavefunction is used, the column is headed: H. and G. coefficients. When only a single Slater function is used for the atomic orbital, the appropriate value of α is entered at the head of the column.

TABLE III. Overlap integrals in units of 10^{-4}.

Molecule number	Naphthalene	Anthracene	Biphenyl	Terphenyl	Quaterphenyl
		Hole			
2	−0.31	0.76	42.63	23.79	14.85
3	51.14	51.84	−34.07	−36.78	−39.25
4	2.36	0.26	−0.18	−0.08	−0.04
5	−0.30	−0.24	0.67	0.65	0.56
6	−8.20	3.33	2.48	0.00	0.00
7	−0.48	−0.06	0.04	0.01	0.01
8	−0.06	0.03	1.78	0.00	0.00
9	−24.17	34.98	−12.21	−1.02	4.12
10	21.46	−17.27	−18.34	−0.01	−0.01
11	0.04	−0.02	0.02	−10.24	−7.50
12	0.00	0.00	0.00	1.22	0.64
13	0.00	0.00	0.00	0.11	0.06
14	−0.07	−0.03	0.00	0.00	0.00
		Electron			
2	1.45	1.04	1.91	9.92	−2.13
3	−8.63	−25.73	−43.31	−0.26	68.09
4	−0.20	0.04	−0.03	0.17	−0.06
5	0.08	−0.22	−0.30	0.04	−0.66
6	−1.71	0.62	−0.62	0.00	0.00
7	0.08	−0.03	−0.03	0.01	−0.21
8	0.03	−0.02	−0.02	0.00	0.00
9	18.84	46.84	18.35	33.34	24.27
10	1.62	−0.68	7.07	−0.18	0.06
11	0.05	−0.03	0.12	−7.42	4.31
12	0.00	0.00	0.00	0.70	−0.22
13	0.00	0.00	0.00	0.05	−0.01
14	−0.02	0.00	0.00	−0.02	0.00

Molecule number	Naphthalene (H. and G. coefficients)	Anthracene (H. and G. coefficients)	Anthracene $\alpha=3.072$	Naphthalene $\alpha=3.08$	Anthracene $\alpha=3.08$	Biphenyl $\alpha=3.08$	Terphenyl $\alpha=3.08$
				Hole			
2	−0.31	0.65	−0.040	0.098	−0.040	11.081	6.311
3	51.24	47.34	16.526	12.956	16.219	−8.881	−11.201
4	2.35	0.23	0.003	0.049	0.003	−0.007	−0.004
5	−0.29	−0.02	−0.008	−0.010	−0.007	0.014	0.016
6	−8.11	3.64	0.227	−0.476	0.219	0.090	0.000
7	−0.49	0.00	0.000	−0.006	0.000	0.000	0.000
8	−0.07	0.04	0.001	−0.002	0.001	0.001	0.000
9	−23.34	30.49	13.437	−2.526	13.205	−1.366	0.806
10	2.08	−14.77	−3.859	3.913	−3.779	−2.872	0.000
11	0.05	−0.02	0.000	0.000	0.000	0.001	−1.726
12	0.00	0.00	0.000	0.000	0.000	0.000	0.049
13	0.00	0.00	0.000	0.000	0.000	0.000	0.000
14	−0.07	−0.02	0.000	0.000	0.000	0.000	0.000
				Electron			
2	1.39	0.75	−0.224	0.946	−0.222	0.478	−0.661
3	−9.67	−27.23	−10.807	−3.435	−10.629	−13.069	−18.309
4	−0.25	0.03	0.000	−0.007	0.000	0.003	0.001
5	0.12	−0.02	−0.008	−0.001	−0.007	−0.007	−0.012
6	−1.55	0.35	0.064	−0.132	0.062	−0.034	0.000
7	0.09	−0.02	−0.001	0.001	−0.001	0.000	0.002
8	0.04	−0.02	−0.001	0.001	−0.001	0.000	0.000
9	19.26	47.13	18.299	8.879	17.984	7.697	10.960
10	1.20	−0.20	−0.384	0.493	−0.378	1.474	0.001
11	0.04	−0.02	0.000	0.000	0.000	0.001	1.004
12	0.00	0.00	0.000	0.000	0.000	0.000	−0.021
13	0.00	0.00	0.000	0.000	0.000	0.000	0.000
14	−0.02	0.00	0.000	0.000	0.000	0.000	0.000

TABLE IV. Bandwidths and splitting in c^{-1} direction in units of 10^{-4} eV.

	Two-center integrals only						
	Naphthalene	Anthracene	Biphenyl	Terphenyl	Quaterphenyl	Naphthalene (H. and G. coefficients)	Anthracene (H. and G. coefficients)
			Hole				
a^{-1}_{lower}	20.0	235.5	177.8	56.9	2.4	17.4	235.2
a^{-1}_{upper}	53.9	208.8	155.1	43.0	6.0	55.7	205.4
b^{-1}_{lower}	413.7	670.9	95.3	261.3	355.9	417.6	638.5
b^{-1}_{upper}	380.2	226.6	428.2	361.3	359.6	379.6	198.1
c^{-1}_{lower}	286.2	222.3	546.0	311.4	222.9	275.5	182.1
c^{-1}_{upper}	250.4	256.1	123.1	65.8	21.0	240.1	216.6
$c^{-1}_{\text{splitting}}$	none	444.3	none	none	none	none	440.6
			Electron				
a^{-1}_{lower}	222.8	455.0	238.0	303.2	292.9	225.1	459.4
a^{-1}_{upper}	236.9	451.4	244.9	311.5	299.8	237.8	457.5
b^{-1}_{lower}	142.1	184.8	121.0	193.8	323.0	135.2	177.1
b^{-1}_{upper}	317.5	721.5	603.8	808.3	915.6	327.6	739.7
c^{-1}_{lower}	40.1	15.7	107.9	46.8	43.8	32.7	8.3
c^{-1}_{upper}	15.4	20.7	83.8	83.1	90.4	10.4	11.2
$c^{-1}_{\text{splitting}}$	404.1	906.3	291.1	484.8	458.5	419.9	916.8

	Two- and three-center integrals			Two-center integrals only			
	Naphthalene	Anthracene	Biphenyl	Naphthalene $\alpha=3.08$	Anthracene $\alpha=3.08$	Biphenyl $\alpha=3.08$	Terphenyl $\alpha=3.08$
			Hole				
a^{-1}_{lower}	34	243	223	15.7	57.2	12.4	0.2
a^{-1}_{upper}	59	209	197	17.4	56.4	12.7	0.4
b^{-1}_{lower}	511	757	139	73.5	139.7	52.9	56.0
b^{-1}_{upper}	485	329	524	41.5	35.8	28.7	55.4
c^{-1}_{lower}	311	272	689	30.8	33.1	28.7	15.4
c^{-1}_{upper}	369	314	163	31.6	33.3	69.5	40.9
$c^{-1}_{\text{splitting}}$	none	452	none	none	113.6	none	none
			Electron				
a^{-1}_{lower}	209	491	284	56.4	96.7	51.3	71.0
a^{-1}_{upper}	237	487	293	56.8	96.5	51.4	71.1
b^{-1}_{lower}	131	209	165	37.2	37.3	20.7	33.2
b^{-1}_{upper}	316	775	690	76.0	159.1	112.6	161.4
c^{-1}_{lower}	34	17	105	10.0	6.8	14.7	5.0
c^{-1}_{upper}	20	22	102	0.9	4.0	8.1	10.9
$c^{-1}_{\text{splitting}}$	392	979	369	102.2	193.3	79.8	126.2

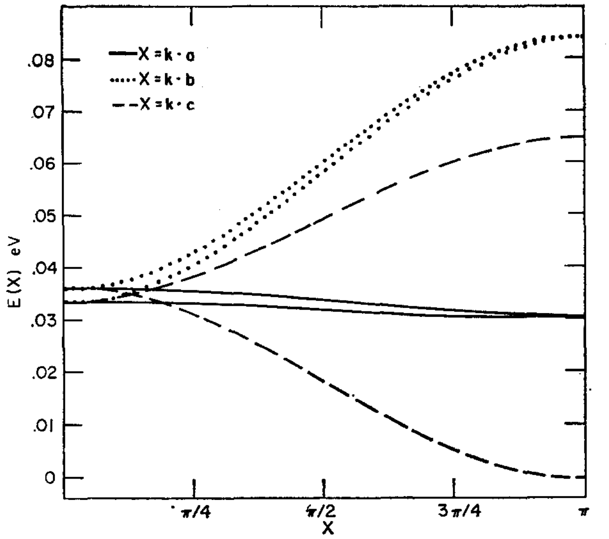

FIG. 3. Shape of the excess hole band of naphthalene in the $\mathbf{a}^{-1}$ (solid line), $\mathbf{b}^{-1}$ (dotted line), and $\mathbf{c}^{-1}$ (dashed line) directions.

It should be noted that for all the compounds considered the electron band splits appreciably in the $\mathbf{c}^{-1}$ direction. In all cases the hole band either does not split or has a much smaller splitting. The $\mathbf{a}^{-1}$ and $\mathbf{b}^{-1}$ bands meet at $\pi\mathbf{a}^{-1}$ and $\pi\mathbf{b}^{-1}$ as we have shown. At $\mathbf{k}=\pi\mathbf{a}^{-1}$ and $\pi\mathbf{b}^{-1}$, the two bands are expected to be degenerate. Because of the existence of a twofold screw axis in the **b** direction and a glide plane in the **a** direction, the group of **k** has only a two-dimensional irreducible representation at $\mathbf{k}=\pi\mathbf{a}^{-1}$ and $\pi\mathbf{b}^{-1}$.[32]

Obviously, the calculation described herein is very sensitive to the form of the wavefunction. A 1% change in the orbital exponents produces a 10% to 15% change in the resonance integrals. We do not claim our numbers are accurate to better than a multiplicative factor of 2 or 3, but we do feel that it cannot be denied that the bandwidths in anthracene and related compounds (about 0.01 to 0.1 eV) are about five times larger than those found by LeBlanc.

The largest predicted splitting of the electron bands in the $\mathbf{c}^{-1}$ direction is for anthracene (0.1 eV). This splitting is large enough compared to kT to be readily observed at room temperature if a suitable experiment could be designed.

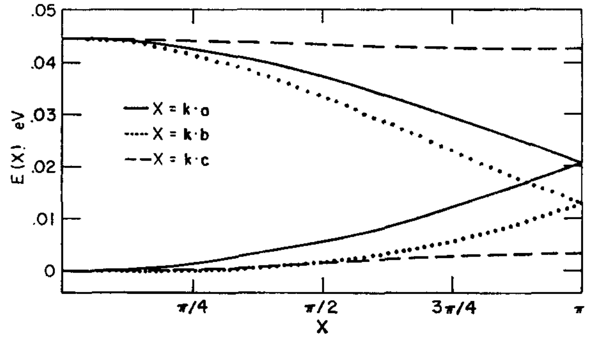

FIG. 4. Shape of the excess electron band of naphthalene in the $\mathbf{a}^{-1}$ (solid line), $\mathbf{b}^{-1}$ (dotted line), and $\mathbf{c}^{-1}$ (dashed line) directions.

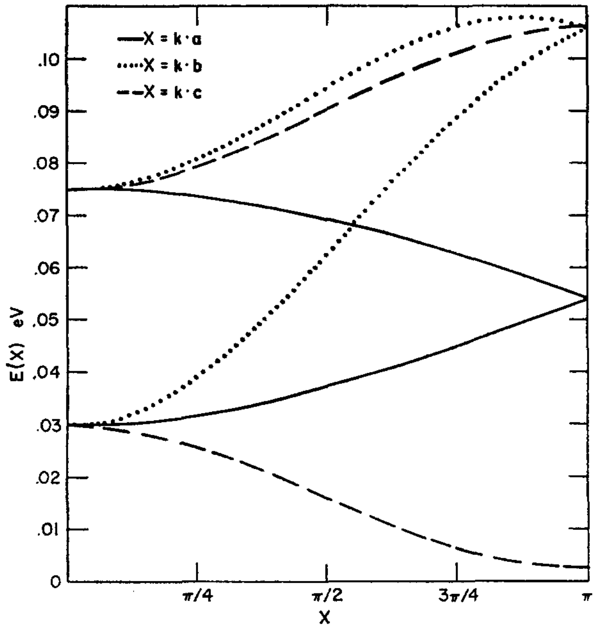

FIG. 5. Shape of the excess hole band of anthracene in the $\mathbf{a}^{-1}$ (solid line), $\mathbf{b}^{-1}$ (dotted line), and $\mathbf{c}^{-1}$ (dashed line) directions.

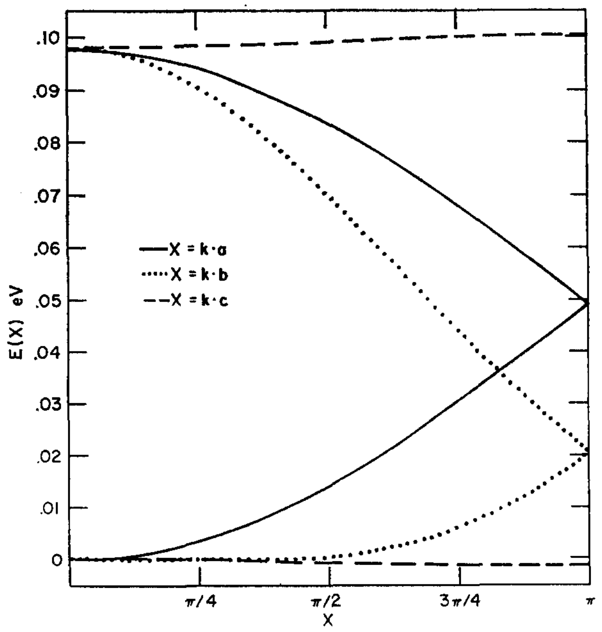

FIG. 6. Shape of the excess electron band of anthracene in the $\mathbf{a}^{-1}$ (solid line), $\mathbf{b}^{-1}$ (dotted line), and $\mathbf{c}^{-1}$ (dashed line) directions.

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[32] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, New York, 1960), Chap. VI.

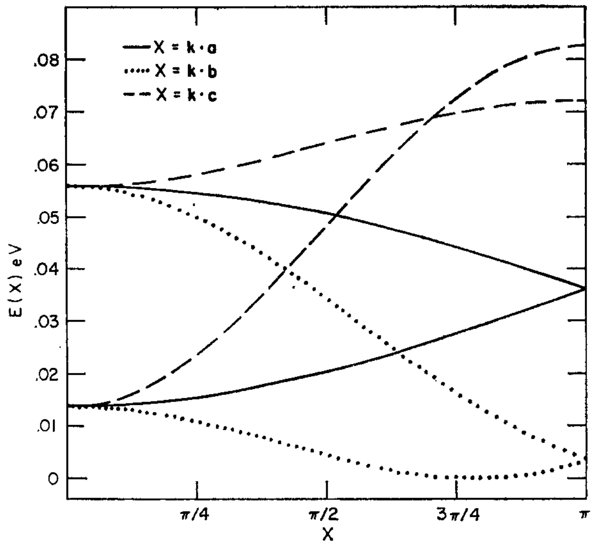

FIG. 7. Shape of the excess hole band of biphenyl in the $\mathbf{a}^{-1}$ (solid line), $\mathbf{b}^{-1}$ (dotted line), and $\mathbf{c}^{-1}$ (dashed line) directions.

Besides all the other approximations already mentioned, we have, it should be noted, neglected polarization and vibration effects. It is not clear whether these effects would increase or decrease the bandwidth.

VI. MOBILITY CALCULATIONS

The evaluation of the mobility tensor was carried out in the relaxation (or collision) time[33] approximation. Two simplified models for the relaxation time were considered: (a) constant isotropic relaxation time, i.e., $\tau(\mathbf{k})=\tau_0$; (b) constant isotropic free path $\lambda=\tau(\mathbf{k})\,|\mathbf{v}(\mathbf{k})|$. Here $\mathbf{v}(\mathbf{k})$ is the group velocity associated with $\Psi(\mathbf{k})$ and related to the energy bands by

$$\mathbf{v}(\mathbf{k})=(1/\hbar)\nabla_k E(\mathbf{k}). \tag{32}$$

The mobilities calculated by these methods involve either the constant relaxation time or the constant free path as a parameter. These parameters may be estimated by comparing the calculated mobility values with the experimental data. Such comparison may provide *ad hoc* justification for a treatment of the conductivity in the framework of the band theory of charge carriers.

We choose an orthogonal coordinate system whose axes are parallel to the **a** and **b** unit cell vectors and the vector $\mathbf{c}'$ (i.e., $\mathbf{c}^{-1}$) which is perpendicular to the *ab* plane. The components of mobility tensor are

$$\mu_{ij}=e\tau_0\langle v_iv_j\rangle/kT, \tag{33}$$

and

$$\mu_{ij}=(e\lambda/kT)\langle v_iv_j/|\mathbf{v}(\mathbf{k})|\rangle, \tag{34}$$

for the constant relaxation time and constant free path approximations, respectively. In the above equations v_i as the ith component of the velocity vector $\mathbf{v}(\mathbf{k})$ and the bracket indicates an average over the Boltzmann distribution of electrons in the energy bands. Thus

$$\langle v_iv_j\rangle=\int\left\{\frac{\partial E_+}{\partial k_i}\frac{\partial E_+}{\partial k_j}\exp(-\beta E_+(\mathbf{k})]+\frac{\partial E_-}{\partial k_i}\frac{\partial E_-}{\partial k_j}\exp[-\beta E_-(\mathbf{k})]\right\}d\mathbf{k}\Big/\hbar^2\int\{\exp[-\beta E_+(\mathbf{k})]+\exp[-\beta E_-(\mathbf{k})]\}d\mathbf{k}, \tag{35}$$

where $\beta=1/kT$. The reader should note that the energy of a hole is measured downward from the top of the band. For convenience, both the zeros and the sign of the energy in Figs. 3, 5 and 7 have been changed.

Since the bandwidths are of the order of several kT at room temperature, the average values of $\langle v_iv_j\rangle$ and $\langle v_iv_j/|\mathbf{v}(\mathbf{k})|\rangle$ over the bands were calculated numerically. Evaluation of mobility tensors for the cases of constant relaxation time and constant free path were carried out simultaneously applying the trapezoidal integration rule (using $12^3=1728$ integration points) on an IBM 7090 computer. Such calculations, for both the electron and hole for a given compound, require only 2 min of computer time. Errors inherent in the numerical integrations are probably in the fifth decimal place and thus are very much smaller than the errors introduced by the approximations made.

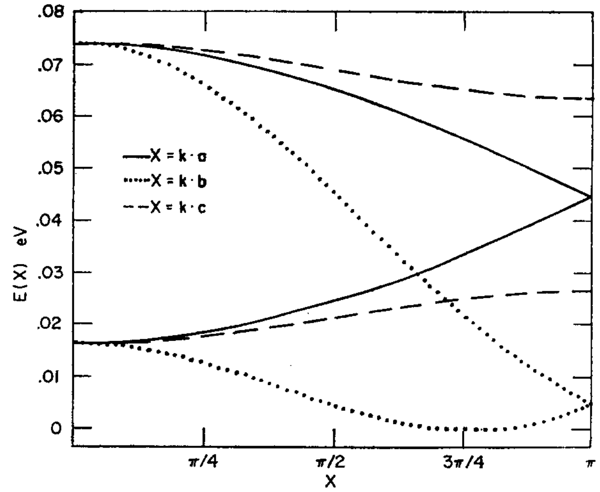

FIG. 8. Shape of the excess electron band of biphenyl in the $\mathbf{a}^{-1}$ (solid line), $\mathbf{b}^{-1}$ (dotted line), and $\mathbf{c}^{-1}$ (dashed line) directions.

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[33] F. J. Blatt, Solid State Phys. **12**, 199 (1961).

TABLE V. Components of the mobility tensor in the constant-free-time approximation in units of 10^{10} cm^2/sec^2.

	Naphthalene				Anthracene			
		2-center integrals H. and G.				2-center integrals H. and G.		
	2- and 3-center Hückel 4 α's	Hückel 4 α's	Coeff. 4 α's	Hückel $\alpha=3.08$	2- and 3-center Hückel 4 α's	Hückel 4 α's	Coeff. 4 α's	Hückel $\alpha=3.08$
				Hole				
$\langle V_a^2\rangle$	14	9	8	0.006	87	79	71	5.3
$\langle V_b^2\rangle$	217	146	147	3.46	251	191	170	9.5
$\langle V_{c'}^2\rangle$	28	18	17	0.30	29	21	15	0.6
$\langle V_aV_c'\rangle$	3	2	2	0.04	11	8	6	0.2
				Electron				
$\langle V_a^2\rangle$	39	42	43	2.80	186	163	162	9.8
$\langle V_b^2\rangle$	25	26	28	1.81	119	107	111	8.4
$\langle V_{c'}^2\rangle$	1	0.8	0.7	0.04	0.3	0.3	0.1	0.02
$\langle V_aV_c'\rangle$	−0.5	−0.5	−0.4	−0.02	0.05	0.04	0.01	0.005

	Biphenyl			Terphenyl		Quaterphenyl
		2-center integrals		2-center integrals		2-center integrals
	2- and 3-center Hückel 4 α's	Hückel 4 α's	Hückel $\alpha=3.08$	Hückel 4 α's	Hückel $\alpha=3.08$	Hückel 4 α's
			Hole			
$\langle V_a^2\rangle$	16	11	0.12	4.2	0.07	5.7
$\langle V_b^2\rangle$	98	69	1.55	87	2.85	112
$\langle V_{c'}^2\rangle$	424	267	6.22	178	4.19	131
$\langle V_aV_{c'}\rangle$	−38	−24	−0.57	5.5	0.14	13
			Electron			
$\langle V_a^2\rangle$	35	25	1.88	41	4.04	33
$\langle V_b^2\rangle$	139	115	4.24	199	9.28	283
$\langle V_{c'}^2\rangle$	0.2	0.6	0.03	1.5	0.05	4.9
$\langle V_aV_{c'}\rangle$	−0.4	−0.4	−0.01	0.05	0.00	0.02

It should be noted that the mobility anisotropy derived from the present approximations contains only the contributions from the anisotropy in the energy bands. In Tables V and VI we present the components of the mobility tensor at 300°K (not including the constant multiplicative factors $e\tau_0/kT$ and $e\lambda/kT$) calculated assuming constant free time and constant free path, respectively. For naphthalene, anthracene, and biphenyl, we list the mobility components evaluated from the energy bands which include the contributions of the three-center integrals and those in which two-center integrals only were included. For terphenyl and quaterphenyl only mobility values for the "two-center integral" bands are listed. The mobility components which are not listed are at least 100 times smaller than the smallest terms in Tables V and VI.

In order to show the effect of the tail part of the atomic orbitals used, we also give the components of the mobility calculated from the bands which result from the single Slater-type atomic orbital with its exponent, $\alpha=3.08$. These values are different from the values of LeBlanc and Thaxton *et al.* This difference primarily arises because our method differs from theirs in two points: (i) a minor mistake in Eqs. (A10) and (A11) of LeBlanc's paper was corrected in deriving

TABLE VI. Components of the mobility tensor in the constant-free-path approximation in units of 10^6 cm/sec.

	Naphthalene				Anthracene			
		2-center integrals H. and G.				2-center integrals H. and G.		
	2- and 3-center Hückel 4 α's	Hückel 4 α's	Coeff. 4 α's	Hückel $\alpha=3.08$	2- and 3-center Hückel 4 α's	Hückel 4 α's	Coeff. 4 α's	Hückel $\alpha=3.08$
				Hole				
$\langle V_a^2/\lvert V\rvert\rangle$	0.9	0.7	0.6	0.004	4.2	4.2	4.1	1.28
$\langle V_b^2/\lvert V\rvert\rangle$	11.6	9.6	9.7	1.58	11.1	9.5	9.0	2.09
$\langle V_{c'}^2/\lvert V\rvert\rangle$	1.9	1.5	1.4	0.18	1.6	1.3	1.0	0.18
$\langle V_aV_{c'}/\lvert V\rvert\rangle$	0.2	0.2	0.2	0.02	0.5	0.4	0.3	0.03
				Electron				
$\langle V_a^2/\lvert V\rvert\rangle$	4.3	4.5	4.5	1.18	9.4	8.8	8.7	2.11
$\langle V_b^2/\lvert V\rvert\rangle$	3.0	3.0	3.1	0.85	5.9	5.7	5.8	1.75
$\langle V_{c'}^2/\lvert V\rvert\rangle$	0.2	0.1	0.1	0.02	0.05	0.04	0.02	0.007
$\langle V_aV_{c'}/\lvert V\rvert\rangle$	−0.04	−0.04	−0.04	−0.008	0.01	0.01	0.003	0.001

	Biphenyl			Terphenyl		Quaterphenyl
		2-center integrals		2-center integrals		2-center integrals
	2- and 3-center Hückel 4 α's	Hückel 4 α's	Hückel $\alpha=3.08$	Hückel 4 α's	Hückel $\alpha=3.08$	Hückel 4 α's
			Hole			
$\langle V_a^2/\lvert V\rvert\rangle$	0.7	0.6	0.05	0.34	0.03	0.43
$\langle V^2/\lvert V\rvert\rangle$	4.8	4.1	0.62	5.4	1.05	6.8
$\langle V_{c'}^2/\lvert V\rvert\rangle$	16.1	12.7	1.98	9.9	1.46	7.8
$\langle V_aV_{c'}/\lvert V\rvert\rangle$	−1.4	−1.1	−0.18	0.30	0.05	0.77
			Electron			
$\langle V_a^2/\lvert V\rvert\rangle$	2.5	2.0	0.75	2.5	1.05	1.7
$\langle V_b^2/\lvert V\rvert\rangle$	9.1	8.4	1.49	11.0	2.16	13.7
$\langle V_{c'}^2/\lvert V\rvert\rangle$	0.02	0.08	0.18	0.19	0.02	0.47
$\langle V_aV_{c'}/\lvert V\rvert\rangle$	−0.03	−0.04	−0.003	0.003	0.00	−0.01

Eq. (28); (ii) in averaging over the distribution in bands we did not neglect the Boltzmann factor.

As can be seen from comparing these results with the experimental data (Table VII), the anisotropy of the mobility calculated from the Clementi–Roothaan SCF wavefunction for the carbon $2p$ atomic orbital is in better agreement with experimental values than the mobility calculated from the single Slater-type atomic orbital with $\alpha=1.625$ a.u. Although one does not expect good agreement with the experimental data, we observe that our calculated values of the mobility anisotropy are definitely in better agreement with the experimental data for naphthalene[34] and anthracene (which are the only available data) than the previous calculations.

It is important to note that the anisotropy in the *ab* plane of the hole mobility in naphthalene cannot be appropriately described in terms of LeBlanc's treatment, while the present calculations lead to quite reasonable agreement between theory and experiment.

The mobility anisotropy is determined in the present scheme by the crystal geometry and the symmetry of the molecular wavefunctions. The difficult problem of the dependence of the mobility anisotropy on the possible anisotropy of the relaxation time should be included in a more refined treatment.

The present treatment can be used to account for the pressure dependence of the electron and hole mobilities in anthracene, as studied experimentally by Kepler. The mobility change is due to the change of unit-cell dimensions with compression. The compressibility of anthracene was studied by Bridgeman[34]; however, the anisotropy of the compressibility is unknown. For the purpose of making an order of magnitude calculation, it was assumed that the application of a pressure of 3000 atm leads to a uniform decrease of 1% of the unit-cell dimensions without changing the angles. The pressure effect on the mobility calculated using the mean free time approximation is presented in Table VIII. It is apparent that the change in the unit cell dimensions is the predominant factor accounting for the pressure dependence of the mobility. If the carrier scattering mechanism involves acoustical phonons, the pressure dependence of the Debye temperature of the crystal will affect the relaxation time. However, a crude estimate of this effect indicates that it is quite small.[11b]

The temperature dependence of the mobility is difficult to discuss in terms of the crude scattering models used herein. At least three effects can be discerned: (a) the relaxation time is temperature-dependent because of the temperature dependence of the average phonon density of each vibrational mode; (b) the thermal expansion of molecular crystals is large, being about 3% from 77° to 300°K. As seen from the calculation of the pressure dependence of the mobility, the magnitude of the mobility is quite sensitive to the relative separation of the molecules; (c) the distribution of electrons within the bands is sensitive to temperature because the bandwidth exceeds kT at ordinary temperatures. Numerical calculations show that Effect (b) leads to a decrease of the mobility with increasing temperature in a manner analogous to the pressure effect. Effect (c) leads to a comparable effect in the opposite direction. Kepler's experimental results[11] indicate that Effect (a) is of predominant importance in accounting for the temperature dependence of the mobility.

Finally, we must consider the adequacy of the band model to account for electron and hole mobilities in aromatic molecular crystals. The band model will be valid only if the uncertainty in the energy of the scattered carriers does not exceed the bandwidth W. If τ is the average relaxation time for a carrier scattered between states of different crystal momentum, the criterion for the applicability of the band model is given by $W \geq \hbar/\tau$. From Eq. (33), using the experimental values for the mobility in the *ab* plane of anthracene, it follows that the relaxation time is 1.3×10^{-14} sec for hole and 2.4×10^{-14} sec for electrons. Thus $\hbar/\tau$ has an average value of 0.05 and 0.03 eV for excess holes and electrons, respectively, which are of the order of the calculated bandwidths. From Eq. (34) and the experimental mobilities, one estimates mean free paths of 3.5 Å for holes and 4.5 Å for electrons in the *ab* plane in anthracene. These mean free paths are of the same order of magnitude as the lattice constants. This raises the question of whether the band model is the best approach to account for carrier mobility in these systems. The system of excess electrons or holes in molecular crystals is probably an intermediate case between the weak scattering approximation, where the delocalized Bloch states have a long lifetime and the strong scattering approximation where the localized states are dominant. If the band description of the charge carrier is applicable to these systems, we are led to conclude that the next most important problem to be considered in understanding the mobility of charge carriers is the mechanism and magnitude of interaction of the charge carrier with intramolecular and intermolecular vibrations. Such a study will also provide further information on the anisotropy of the mobility and must be coupled with an investigation of the effects of vibration and polarization on bandwidth.

TABLE VII. Experimentally measured components of the mobility tensor in cm²/V·sec.

	Naphthalene[a]		Anthracene[11b]	
	Hole	Electron	Hole	Electron
μ_{aa}	0.9	0.7	1.0	1.7
μ_{bb}	1.4	0.7	2.0	1.0
$\mu_{c'c'}$	0.4	0.4	0.8	0.4

[a] M. Silver, J. R. Rho, and R. C. Jarnigan, J. Chem. Phys. (to be published).

TABLE VIII. The pressure dependence of the electron and hole mobility in anthracene.[a]

	Electron		Hole	
	μ(3000 atm)/μ(1 atm)		μ(3000 atm)/μ(1 atm)	
Crystal direction	Exptl.	Calc.	Exptl.	Calc.
a	1.4	1.1	1.4	1.0
b	1.3	1.2	1.4	1.1
c'	1.0	0.9	1.4	1.3

[a] The experimental data are taken from Ref. 11(b).

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[34] P. W. Bridgeman, Proc. Am. Acad. Arts Sci. 76, 20 (1944).