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BAND STRUCTURE OF ANTHRACENE AND NAPHTHALENE: SURFACE STATES AND ELECTRIC FIELD EFFECTS

by

Peter S. Stern

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Abstract

BAND STRUCTURE OF ANTHRACENE AND NAPHTHALENE: SURFACE STATES AND ELECTRIC FIELD EFFECTS

by

Peter S. Stern

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The effect of an applied electric field (10^4 - 10^5 V/cm) on the energy bands of anthracene has been investigated to first and second order using perturbation theory. The energy of the bands and the splitting between plus and minus bands does not change in any case by more than 0.1 - 0.2%, and the conductivity is, therefore, not expected to change appreciably.

The energy bands for each of the three surfaces of anthracene and naphthalene have been calculated using a direct crystal orbital approach. The tight-binding approximation is employed and the crystal wave function is made up of a linear combination of molecular wave functions constructed from a linear combination of carbon 2 p_z wave functions using Hückel coefficients. Separated surface bands have been found for naphthalene in the ac and bc planes, and the carrier mobility has been calculated for these. It is found to be much greater than the bulk mobility in the ac band, but not in the bc band. No separated surface bands were found for anthracene, although isolated surface states have been found for both anthracene and naphthalene.

The effect of a perturbation on the surface bands of anthracene and naphthalene has also been calculated. It is found that perturbations of the order of 10 - 25% will effect separation of naphthalene surface bands in the ab plane, but that for anthracene, surface bands are not readily caused to separate from the bulk bands.

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I. INTRODUCTION

A great deal of study has been devoted to the electronic properties of molecular crystals in the past twenty years, particularly anthracene and naphthalene, much of it spurred by the suggestion of Albert Szent-Györgi in 1941(1) that these types of large aromatic molecules are implicated in biological processes involving electron transfer. Since then, a considerable amount of work has been devoted to testing the validity of that suggestion. Szent-Györgi himself found photoconduction in certain colored protein films in 1946,(2) while in 1948, Eley found semiconductor behavior in the conductivity of some of the phthalocyanines.(3) In 1949, Katz suggested that the primary act of photosynthesis involves the photoconduction of chlorophyll systems,(4) and further work in this area was done by Bradley and Calvin(5) and Nelson(6) who detected photoconduction in solid chlorophyll. The role of photoconduction in vision has also been explored.(7 - 10) Although the validity of the application of semiconductor concepts to other biological and biochemical phenomena is somewhat in doubt, the work that has been done has touched upon such areas as the cytochrome chain in respiration,(11) the glycolytic cycle,(12) carcinogenesis,(13 - 15) nerve impulse transmission,(13, 16) protein structures,(17 - 19) DNA,(15, 20) and bimolecular lipid membranes,(21) to name just a few. In the past five years a number of extensive reviews in the area of organic semiconductors have been written, containing extensive bibliographies of the research done in this field.(22 - 25) One of the major areas of interest which has not had adequate theoretical treatment is that of the existence of surface states and their contribution to the electronic properties of organic semiconductors.(25) It is the purpose of this work to attempt to explore the possibility of the existence of surface states in anthracene and naphthalene, and to see what their role might be in the electronic properties of these crystals.

A. Organic semiconductors and band theory

Dielectric materials can be placed in three general classes defined by their conductivities. Metals are characterized by conductivities of the order of 10^2 to 10^8 (ohm cm)$^{-1}$ with a carrier concentration of $10^{22}/cm^3$ and a mobility of 10^3 cm^2 (volt sec)$^{-1}$. Insulators have conductivities from 10^{-22} to 10^{-14} (ohm cm)$^{-1}$ and carrier concentrations below $10^9/cm^3$. Between these two lies the important class of materials known as semiconductors. Within this group there are both inorganic and organic semiconductors. Our interest here will be with the latter which have conductivities in the range 10^{-14} to 10^2 (ohm cm)$^{-1}$, carrier concentrations of 10^6 to $10^{19}/cm^3$ and mobilities of 10^{-6} to 10^2 cm^2 (volt-sec)$^{-1}$. According to this definition, anthracene and naphthalene would both be insulators except for the probability of photoinjection or surface injection of carriers which places their conductivity in the appropriate range for semiconductors. This point is discussed further below.

The conductivity σ is the charge transported across a unit cross-sectional area per second per unit applied electric field and can be written as

$$\sigma = z\ e\ n\mu \tag{1}$$

where z is the number of electronic charges per carrier, e is the electronic charge, n is the carrier concentration in cm^{-3}, and μ, the mobility, is the velocity of charge transport per unit electric field in cm^2 $(\text{volt-sec})^{-1}$. The units of σ then are $(\text{ohm cm})^{-1}$ which is seen to be the reciprocal of the resistivity, the resistance per unit cube. In general, the mobility μ may be anisotropic and so the conductivity may also be anisotropic.

The organic semiconductors of interest here are those which fall into the category known as molecular crystals. This nomenclature refers to those crystals which are weakly bonded by Van der Waals forces so that to a first approximation a description of the crystal is made in terms of a collection of individual molecules which retain their molecular properties. Any collection of molecules making up a periodic crystal structure results in electronic energy bands(26) which serve to explain the conduction properties of these crystals. This is true both for metals and insulators, as well as for semiconductors, and, in fact, the band theory predicts the nature of the conducting material.

If two atoms of hydrogen are brought together, the overlapping of their wave functions, Ψ_A and Ψ_B, results in the formation of two new wave functions

$$\Psi_{\pm} = \Psi_A^1 \Psi_B^2 \pm \Psi_A^2 \Psi_B^1 \qquad (2)$$

where 1 and 2 denote the electrons. Ψ_+, the symmetric orbital, has a lower energy than the two separated atoms and is, therefore, called a bonding orbital while Ψ_-, the antisymmetric orbital, has a greater energy than the two separated atoms and is called an antibonding orbital. By bringing together a large number of atoms, N, at the close distance found in a crystal, each energy level of the atoms is split into N levels; but since N is of the order of Avogadro's number, 10^{23}, the spacing between the levels is so small that the levels form a band of energies. The valence levels in the atom produce a valence band filled with valence electrons while the higher levels produce a conduction band which is separated from the valence band by an energy gap and is normally empty (since in the atoms the higher levels are empty at moderate temperatures). In metals, the highest energy band containing electrons is either only partially filled or overlaps with another empty band so that the electrons are free to move in an electric field. The conductivity that results is very high since the number of electrons is also of the order of 10^{23}. In insulators there are no electrons available to carry the current since at zero temperature the valence band is completely filled and is separated from the empty conduction band by an energy of several electron volts. Since the number of electrons in the conduction band is proportional to exp $(-E/2kT)$, where E is the energy gap separating the bands, a material with a filled valence band separated from the empty conduction band by a small energy gap of about one electron volt allows for the possibility of thermal excitation of some of the valence electrons into the conduction band, and these are then free to carry the current. At the same time, the resultant vacancies left in the valence band are also free to move about and carry current. These free electrons and positively charged holes, then, are the carriers which provide the electronic conductivity to organic semiconductors, and because their number is much lower than the free electrons in metals, the conductivity of semiconductors is much less.

One more distinction between the types of conductivity of semiconductors may be made. An intrinsic semiconductor is one, as described above, in which an electron in some way acquires enough energy to cross the energy gap or forbidden zone. An extrinsic semiconductor is one in which the conductivity is due to some sort of lattice defect. This defect may be in the form of a disruption of the periodicity of the lattice by an excess or deficiency of constituent atoms from the stoichiometric formula or from an impurity with one extra or one less valence electron than the normal lattice atoms. In any case, the effect of the defect is to introduce an energy level within the forbidden zone of the crystal. Depending upon the nature of the defect and the position of the level, this level can as a result of thermal excitation either donate an electron to the conduction band or receive one from the valence band leaving a hole. Either case results in a conductivity for the crystal.

B. Molecular crystals and tight-binding

This concept of band theory can readily be extended to molecular crystals. The individual molecules making up the lattice sites in the crystal are weakly bonded and can be treated as individual species interacting to form energy bands. Using the one-electron approximation of Bloch(27) a single electron wave function is given by

$$\Psi_k = \phi_k (\vec{r}) \exp (i\vec{k}\cdot\vec{r}) \tag{3}$$

where $\vec{k}$ is the wave number of the electron ($|\vec{k}| = 2\pi/\lambda$, λ being its wave length), $\vec{r}$ is the position vector of the electron in the crystal, and ϕ_k is a wave function with the translational periodicity of the crystal. The field on an electron in a solid is made up of three Hartree-Fock operator terms,

$$V = V_1 + V_2 + V_3 \tag{4}$$

where V_1 is the field acting on electron 1 arising from all the nuclei, V_2 is the coulomb potential of the charge distribution and V_3 is the exchange term. In the one-electron model, the coulomb interactions between the valence electrons are ignored and V is assumed to be constant. These approximations lead to the free electron gas model of metals, where the solutions to the Schrödinger equation are of the form (3) with $\phi_k(\vec{r})$ constant, and give an energy $\epsilon(\vec{k})$ for the electron of

$$\epsilon(\vec{k}) = (\hbar^2/2m)\vec{k}^2 \qquad (5)$$

It is obvious that in order for the energy to be real and positive, $\vec{k}$ must be real. The energy levels are very closely spaced so that the energy is almost continuous (e.g. a particle in a box of macroscopic dimensions), and separated bands do not appear.

For the case of interest, that of organic semiconductors, the potential is periodic and, therefore, the solutions to the Schrödinger equation are given by equation (3) with $\phi_k(\vec{r})$ treated essentially as a molecular wave function with translational periodicity. $\phi_k(\vec{r})$ varies within the unit cell of the crystal, but falls off between cells resulting in the condition known as the "tight-binding" approximation.$^{(28)}$ This is a consequence of the fact that the energy of interaction of an electron with a molecule in a molecular crystal is much greater than the energy of interaction between neighboring molecules in the crystal. The same sort of approximation has been applied to the tightly bound inner shell electrons in ionic and valence crystals. The resultant bands are of width of the order of kT, where T is 300°K, and contain N levels, where N is the number of molecules in the crystal, each level capable of being occupied by two electrons. Therefore, if the molecular energy level in the individual molecule contains two electrons the band will be full, whereas if it contains only one electron, the band will be only half filled.

For a molecule such as anthracene or naphthalene, the energy levels can be described by using molecular orbital (MO) theory. Only the delocalized π electrons are dealt with, and these are placed in the lowest molecular orbitals constructed from linear combinations of the atomic 2_{Pz} carbon wave functions. In Hückel(29) MO theory the coefficients for the linear combinations making up the various MO's are found by solution of a secular determinant. For an aromatic ring made up of 14 carbon atoms such as anthracene, there are 14 MO's. The seven that are lowest in energy are completely filled with the 14 π electrons and are bonding orbitals, while the seven of higher energy are empty and are anti-bonding orbitals. In the tight-binding approximation, the valence band is constructed from a linear combination of the highest bonding orbitals of the various anthracene molecules in the lattice, while the conduction band arises from a linear combination of the lowest anti-bonding orbitals.

C. Experimental work on anthracene and napthalene crystals.

At this point, a brief outline of some of the experimental data and theoretical interpretations of the electronic properties of anthracene and naphthalene is presented; however, for a more complete survey of this area one of the reviews cited above(22 - 25) should be consulted. For an intrinsic semiconductor, the conductivity obeys an equation of the form

$$\sigma = \sigma_o \exp(-E/2kT) \tag{6}$$

where E is the energy gap between the valence band and the conduction band and σ_o is called the pre-exponential factor. The pre-exponential factor has been calculated by Helfrich and Riehl.(30) They showed that for intrinsic conductivity, assuming a band model

$$\sigma_o = e(N_{oh}N_{oel})^{\frac{1}{2}} (\mu_h + \mu_{el}) \tag{7}$$

where N_{oh} and N_{oel} are the effective densities of states of the valence and of the conduction band, respectively. μ_h and μ_{el} are the mobilities of the free holes and free electrons, respectively. This reduces to

$$\sigma_o = e\ N_o\ (\mu_h + \mu_{el}) \tag{8}$$

where N_o is the geometric mean of N_{oh} and N_{oel} which are assumed to be approximately equal. Using N_o equal to 4×10^{21} cm^{-3} (about twice the molecular density), and 0.5 cm^2 volt^{-1} sec^{-1} for the sum of the mobilities, σ_o is $3 \times 10^{+2}$ ohm^{-1} cm^{-1}, in good agreement with the experimental value of $1 \times 10^{+2}$ ohm^{-1} cm^{-1}.(31) E is given by

$$E = I_c - A_c \tag{9}$$

where I_c and A_c are the ionization energy and the electron affinity, respectively, of the crystal. For anthracene E is equal to 3.8 ± 0.1 eV.(25) Thus, for anthracene in the solid phase at atmospheric pressure, there can be no measurable intrinsic conductivity. Eley has shown(32) that for a compound with $\mu = 1\ cm^2\ Volt^{-1}\ sec^{-1}$ and N_0 of order $10^{22}\ cm^{-3}$, a conductivity of $10^{-16}\ ohm^{-1}\ cm^{-1}$ (just barely measurable), at 400°K would be expected if E were equal to 2.7 eV. He also concluded, for the same reason, that the dark conductivity of proteins was not intrinsic, and he proposed the existence of surface states as injection sites.(33) He has also discussed various models for surface injection under normal conditions in the dark.(34)

Photoconduction can occur if a photon induces an electronic transition across the energy gap to form a free electron and hole. A number of different processes have been proposed for this transition.(22) In addition to the direct band to band transition, the absorption of a quantum could produce an exciton which could then dissociate (spontaneously, thermally, via a field), to produce carriers. There is considerable evidence(25) for the process involving spontaneous dissociation of an exciton; such a process, called an auto-ionizing transition, can occur if the energy of the exciton is greater than the energy of the band gap. Alternatively the carrier formation can result from a two quantum process such as the collision of a photon with an exciton or the collision of two excitons. Extrinsic photogeneration processes include collision of an exciton with a surface (especially if a molecule such as O_2(35, 36) or I_2(37) is adsorbed), with a dissociation center which traps one of the carriers, and collision of an exciton with an impurity host molecule pair.(22) These processes, in which excitons produce carriers even if their energy is less than E, are called carrier injection. They can occur if one carrier of the electron-hole pair is trapped at an energy sufficiently low, so that the other carrier gains enough energy to be free. Experiments have shown(35, 36) that for all but the most reduced atmospheres, O_2 serves as an electron trap at the surface resulting in hole injection.

D. Summary of research

It would be interesting, therefore, to explore the possibility of surface states in these crystals and what their role might be in facilitating the injection of electrons or holes into the crystal. It would also be of interest to see what surface conductivity might arise as a result of the existence of such surface states and what the effect might be of a charged ion trapped in one of these surface states on the carrier mobilities.

Because of the large fields that would be expected if a charge was trapped on the surface of a crystal, it was decided to first see what the effect would be of a high applied electric field (10^4 - 10^5 V/cm) on the bulk energy bands, and, thereby, on the conductivity of anthracene. Then the energy for each of the three surfaces of both anthracene and naphthalene was calculated to see whether or not surface bands separated from the bulk energy bands. Finally, the effect of an ionic charge (both positive and negative) trapped on the surface on the energy bands of the crystal was considered.

The calculation of the effect of an external electric field on the energy bands of anthracene was carried out by applying perturbation theory to the calculation of the unperturbed energy bands previously carried out by Katz, Rice, Choi, and Jortner.(37) Because of the frequency with which this paper is referred to, it will be designated, hence, as KRCJ. These workers calculated the wave number ($\vec{k}$) dependence of the electron and hole energies of anthracene, naphthalene, and related polyphenyls by employing the tight-binding approximation. This method and the justification for using it to treat molecular crystals have been discussed above. The perturbation due to the electric field, then, is calculated and added on to the unperturbed bands. From these new energy bands the mobility of electrons and holes in the presence of an electric field applied in each of three orthogonal directions can be readily calculated.

The possibility of surface states was first proposed by Tamm,(38) who recognized that in the presence of the surface, a wave function with complex values of $\vec{k}$ may exist. Such a function decreases exponentially from the surface into the bulk and, therefore, leads to a localized state. For a three dimensional crystal, each surface is treated as being infinite in the two directions parallel to the surface and a surface state if it does exist will in fact be a two dimensional band of states separated from the three dimensional band of the bulk crystal. A number of attempts to calculate the surface states of solids made up of individual atoms have been made,(39) but none of these deal with the more complex problem of molecular crystals, in which the crystal lattice is made up of molecules each of which contains a large number of atoms. The method used here is an outgrowth of one used by T. B. Grimley.(40) Again the tight-binding approximation is employed and the crystal wave function is made up of a linear combination of molecular wave functions which are made up of a linear combination of atomic wave functions using Hückel coefficients. The coulomb integrals for the bulk and the three surfaces of both anthracene and naphthalene are calculated, and these, together with the resonance integrals previously calculated by KRCJ, are used to calculate the value of the complex wave number. The energy is then obtained from this and is plotted as a function of k to determine whether or not it overlaps the bulk band. In those cases for which a separated surface band exists, the mobility is calculated within the surface band.

The existence of surface states allows for the possibility of trapping a charged ion on the surface. Such a trapped charge would exert a very high field ($\sim 10^8$ V/cm) on the crystal and could be expected to significantly distort the energy bands. In the case in which a surface band appears that overlaps with a bulk band the perturbation necessary to cause the surface band to separate from the bulk band is calculated.

II. THE EFFECT OF AN ELECTRIC FIELD ON THE EXCESS ELECTRON AND HOLE BAND STRUCTURE OF ANTHRACENE.

The electron and hole band widths for anthracene have been calculated(37, 41, 42) and are of the order of 0.1 eV. It is of interest to determine whether an applied d.c. electric field, of the order of 10^4 to 10^5 volts/cm would alter the width or the slope of either the electron or hole band structure of anthracene enough to increase the carrier mobility.

The applied field was treated as a perturbation to the Hamiltonian for the system and the correction to the $\vec{k}$-dependent portion of the energy was calculated to first and second order. The mobility tensor was calculated from the corrected energy bands.

A. Method of Calculation

The method of calculation of the corrected energy bands parallels that introduced by Le Blanc,(41) used by Thaxton, Jarnagin and Silver,(42) and modified by Katz, Rice, Choi and Jortner (KRCJ)(37) for the energy bands of anthracene. The anthracene crystal belongs to the symmetry group $C_{2h}^5 \equiv P_{2/a}$.(43) A schematic representation of its monoclinic unit cell containing one molecule at the corner, and one molecule at the center of the ab face, is given in Fig. 1. The two molecules of the unit cell are differently oriented, and will result in two energy bands for each electronic state, corresponding to the symmetric and antisymmetric combinations of the wave functions of the molecules in the unit cell. These energy bands are calculated using the tight-binding approximation,(28) since the binding energy of the molecular crystal is very small relative to the excitation energy of the excited electronic states of the molecule.

The one electron crystal wave functions are constructed as Bloch sums(26, 27) of the one electron molecular wave functions, $\emptyset(\vec{r} - \vec{r}_1)$:

$$\Psi_{\pm}(\vec{k}) = \sum_{l=0}^{2N-1} (\pm 1)^l \exp(i\vec{k}\cdot\vec{r}_l)\emptyset(\vec{r}-\vec{r}_l), \tag{10}$$

where l is chosen so that l even labels the corner molecules and l odd the face-center molecules of the unit cell; $\vec{r}_l(\text{odd}) = \vec{r}_{l-1}(\text{even}) + \vec{\beta}$, where $\vec{\beta} = \frac{1}{2}(\vec{a} + \vec{b})$, $\vec{a}$ and $\vec{b}$ being the unit cell vectors in the a and b directions respectively.(37, 44) The wave functions $\emptyset(\vec{r} - \vec{r}_l)$ have two possible orientations in space depending upon whether l is even or odd, and this results in the two different energy bands for the crystal corresponding to $\Psi_+(\vec{k})$ and $\Psi_-(\vec{k})$.

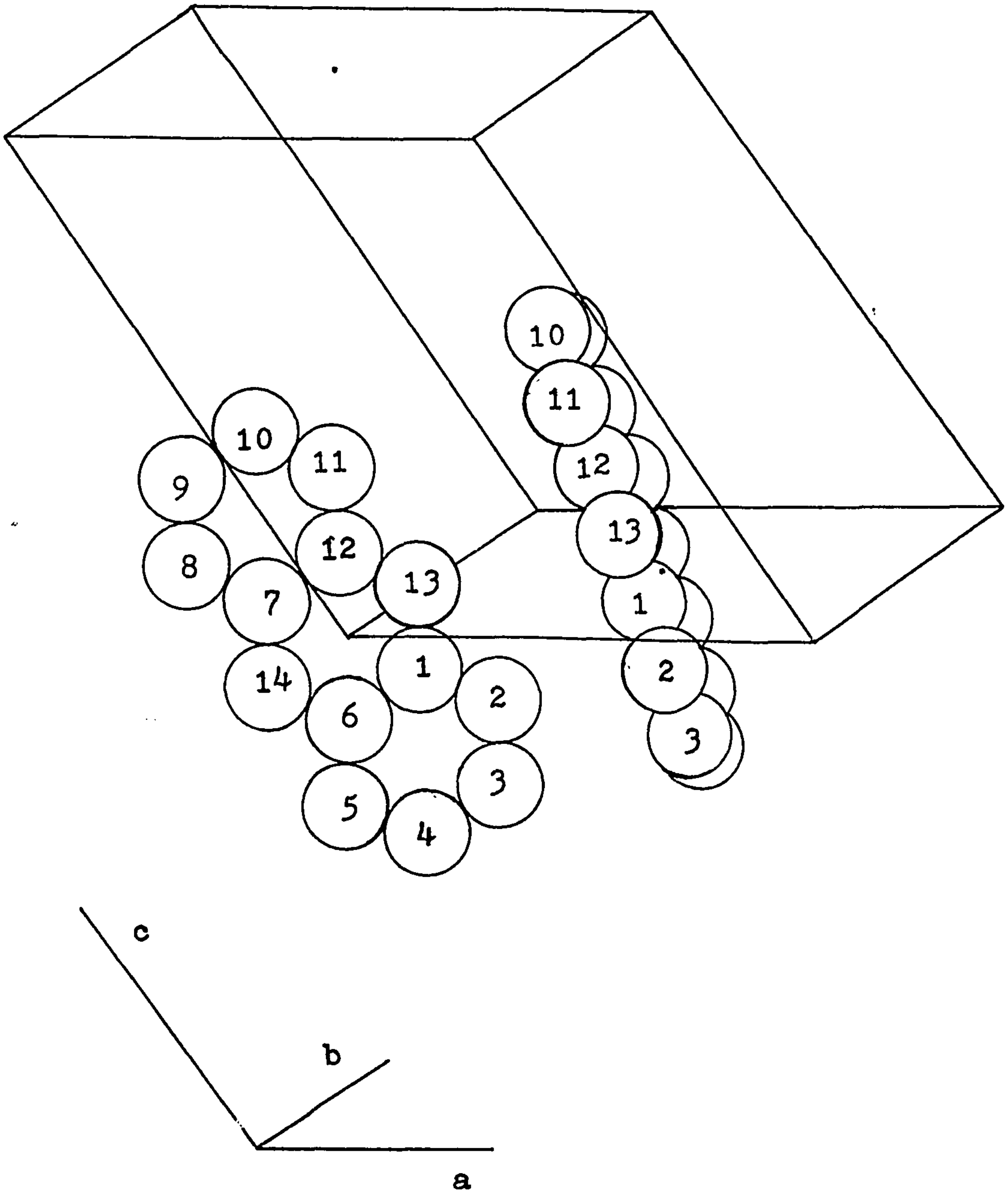


Figure 1. Schematic representation of the unit cell of an anthracene crystal, showing the relative orientation of the two molecules in the unit cell. (After ref. 37)

The Hamiltonian used to find the energy of an excess electron or hole band in the crystal is given by

$$H = (-\hbar^2/2m)\nabla^2 + V(\vec{r}), \tag{11}$$

where $V(\vec{r})$, the potential due to the crystal field, is approximately given by

$$V(\vec{r}) = \sum_n V_n(\vec{r} - \vec{r}_n), \tag{12}$$

and V_n is the Hartree potential of an isolated neutral molecule. The energy of the crystal is:

$$E_{\pm}(\vec{k}) = \langle \Psi_{\pm} | H | \Psi_{\pm} \rangle \ / \ \langle \Psi_{\pm} | \Psi_{\pm} \rangle \ . \tag{13}$$

After substitution of $\Psi_{\pm}(\vec{k})$ from equation (10) and H from equation (11) and (12) into equation (13), one obtains for the energy

$$\begin{aligned} E_{\pm}(\vec{k}) = {} & \sum_{l=0}^{2N-1} \sum_{l=0}^{2N-1} (\pm 1)^{l + l'} \exp\left[-i\vec{k}\cdot(\vec{r}_l - \vec{r}_{l'})\right] \times \\ & \langle \emptyset(\vec{r} - \vec{r}_l) | (-\hbar^2/2m)\nabla^2 + \sum_n V_n(\vec{r} - \vec{r}_n) | \emptyset(\vec{r} - \vec{r}_{l'}) \rangle / \\ & \sum_{l=0}^{2N-1} \sum_{l=0}^{2N-1} (\pm 1)^{l + l'} \exp\left[-ik\cdot(\vec{r}_l - \vec{r}_{l'})\right] \langle \emptyset(\vec{r} - \vec{r}_l) | \emptyset(\vec{r} - \vec{r}_{l'}) \rangle \ . \end{aligned} \tag{14}$$

Substituting the expressions

$$\emptyset_l = \emptyset(\vec{r} - \vec{r}_l), \tag{15}$$

$$H_l^o = (-\hbar^2/2m) \ \nabla^2 + V_l, \qquad (16)$$

and

$$V_n = V(\vec{r} - \vec{r}_n) \qquad (17)$$

into equation (14) reduces it to

$$E_{\pm}(\vec{k}) = \frac{\sum_{l=0}^{2N-1} \sum_{l=0}^{2N-1} (\pm 1)^{l+l'} \exp[-i\vec{k}\cdot(\vec{r}_l - \vec{r}_{l'})] \left(\langle \phi_l | H^o | \phi_{l'} \rangle + \langle \phi_l | {\sum_n}' V_n | \phi_{l'} \rangle \right)}{\sum_{l=0}^{2N-1} \sum_{l=0}^{2N-1} (\pm 1)^{l+l'} \exp[-i\vec{k}\cdot(\vec{r}_l - \vec{r}_{l'})] \ \langle \phi_l | \phi_{l'} \rangle} \cdot \qquad (18)$$

Using the following notations

$$e_o = \langle \phi \,|\, H^o \,|\, \phi \rangle \qquad (19)$$

$$e_n = \langle \phi \,|\, V_n \,|\, \phi \rangle \qquad (20)$$

$$e_l = \langle \phi_l \,|\, V_l \,|\, \phi \rangle \qquad (21)$$

and assuming that

$$\langle \phi(\vec{r}) \,|\, V_n(\vec{r}-\vec{r}_n) \,|\, \phi(\vec{r}-\vec{r}_l) \rangle = 0 \text{ if } n \neq l \neq 0, \qquad (22)$$

and $\langle \phi_l \,|\, \phi_{l'} \rangle = 0$ if $l \neq l'$, (23)

then
$$E_{\pm}(\vec{k}) = \Big\{ e_o + {\sum_n}' e_n + \sum_{l \neq o}^{2N-1} (\pm 1)^l [\exp(i\vec{k}\cdot\vec{r}_l) \langle \phi_o | V_l | \phi_l \rangle + \exp(-i\vec{k}\cdot\vec{r}_l) \ \langle \phi_l | V_l | \phi_o \rangle] \Big\} , \qquad (24)$$

which becomes

$$E_{\pm}(\vec{K}) = e_o + \sum_n{}' e_n + \sum_l{}' (\pm 1)^l \cos(\vec{K}\cdot\vec{r}_l) e_l \qquad (25)$$

where the primes indicate that the sums exclude n = 0 and l = 0.

The assumption that the three center intermolecular integrals (equation (22)) are equal to zero is justified by the very small values of the three center integrals when only two molecules are involved. The integral between the wave function and the potential drops off very rapidly with distance so that the contribution resulting from having the potential on a third molecule is very small. When the overlap integrals (equation (23)) which are of the order of 10^{-4} are multiplied by e_n or e_l, they also become negligible.

Equation (25) may be written as

$$\tilde{E}_{\pm}(\vec{K}) = E_{\pm}(\vec{K}) - e_o - \sum_n{}' e_n = \sum_l{}' (\pm 1)^l \cos(\vec{K}\cdot\vec{r}_l) e_l \qquad (26)$$

since only the cosine term is $\vec{K}$-dependent.

In order to investigate the effects of an electric field on the energy bands of anthracene, it is necessary only to calculate the effect on the $\vec{K}$-dependent portions of E since the mobility is a function of $\partial E/\partial \vec{K}$. This means that the absolute value of the energy is not obtained as was also the case with KRCJ.

To first order, let

$$H = H^{o} + H' \tag{27}$$

$$H' = -e\,\vec{F}\cdot\vec{r} \tag{28}$$

with $\vec{F}$ being the electric field vector. Then

$$E_{\pm}(\vec{k}) = \{\langle\Psi_{\pm}\,|\,H^{o}\,|\,\Psi_{\pm}\rangle + \langle\Psi_{\pm}\,|\,H'\,|\,\Psi_{\pm}\rangle\}/\langle\Psi_{\pm}\,|\,\Psi_{\pm}\rangle\ , \tag{29}$$

or $$E_{\pm}(\vec{k}) = E^{o} + E' \tag{30}$$

where E^{o} is given by equation (25) and E' by the second term in equation (29). Using the approximations of before

$$\tilde{E}'_{\pm}(\vec{k}) = E'_{\pm}(\vec{k}) - e'_{o} - \sum_{n}{}' e'_{n} = \sum_{l}(\pm1)^{l}\cos(\vec{k}\cdot\vec{r}_{l})e'_{l}, \tag{31}$$

where $$e'_{o} = \langle\phi(\vec{r})\,|\,-e\vec{F}\cdot\vec{r}\,|\,\phi(\vec{r})\rangle \tag{32}$$

$$e'_{n} = \langle\phi(\vec{r})\,|\,-e\vec{F}\cdot(\vec{r}-\vec{r}_{l})\,|\,\phi(\vec{r})\rangle \tag{33}$$

$$e'_{l} = \langle\phi(\vec{r}-\vec{r}_{l})\,|\,-e\vec{F}\cdot\vec{r}\,|\,\phi(\vec{r})\rangle\ . \tag{34}$$

Thus it is only necessary to calculate the value of the integrals e'_{l} and add them to the previously computed values of e_{l} (KRCJ) in order to obtain the perturbed band structure of anthracene as a function of $\vec{k}$.

The second order correction to the energy is given by the term

$$E''_{\pm}(\vec{k}) = \left| \langle \Psi'_{\pm} \,|\, -e\vec{F}\cdot\vec{r} \,|\, \Psi_{\pm} \rangle \right|^{2} / \Delta E_{1o} \qquad (35)$$

where $\Psi'_{\pm}$ represents one of the excited states of the crystal and ΔE_{1o} is the difference in energy between $\Psi'_{\pm}$ and the ground state, $\Psi_{\pm}$. For the electron band, the excited states were taken as those bands which resulted from exciting an electron from a lower lying orbital into the electron band, or from the electron band into a higher lying orbital. The excited states of the valence bands were constructed in an analogous manner. For each case, there were only seven symmetry allowed transitions. As before, this problem reduces to that of finding the value of the term $\tilde{E}''_{\pm}(\vec{k})$:

$$\tilde{E}''_{\pm}(\vec{k}) = \sum_{l} (\pm 1)^{l} \cos(\vec{k}\cdot\vec{r}_{l}) \left| e''_{l} \right|^{2} / \Delta e, \qquad (36)$$

$$\text{where} \quad e''_{l} = \langle \emptyset'(\vec{r}-\vec{r}_{l}) \,|\, -e\vec{F}\cdot\vec{r} \,|\, \emptyset(\vec{r}) \rangle \ , \qquad (37)$$

and Δe is the difference in energy between $\emptyset'$ and $\emptyset$. As before, the energies resulting from each term e''_{l} are added to the corresponding zero-field and first-order energies to get the band structure of anthracene to second order.

KRCJ calculated $E_{\pm}(\vec{k})$ by summing over molecules $l = 2$ to 14, numbered as shown in the accompanying diagram

(Fig. 2). This includes all molecules on the corner and side-center of the unit cell, as well as molecule 14, included because of its relatively close position. The nearest neglected molecules then, have no atoms closer than 7.5 Å and the energy as a function of $\vec{k}$ becomes (KRCJ)

$$\begin{aligned}
E_{\pm}(\vec{k}) = 2\Big\{ & e_2 \cos \vec{k}\cdot\vec{c} + e_3 \cos \vec{k}\cdot\vec{b} + e_4 \Big[\cos \vec{k}\cdot(\vec{b}+\vec{c}) + \\
& \cos \vec{k}\cdot(\vec{b}-\vec{c})\Big] + e_5 \cos \vec{k}\cdot\vec{a} + e_6 \cos \vec{k}\cdot(\vec{c}+\vec{a}) + e_7\Big[\cos \vec{k}\cdot(\vec{a}+\vec{b}) + \\
& \cos \vec{k}\cdot(\vec{a}-\vec{b})\Big] + e_8\Big[\cos \vec{k}\cdot(\vec{a}+\vec{b}+\vec{c}) + \cos \vec{k}\cdot(\vec{a}-\vec{b}+\vec{c})\Big] \pm \\
& e_9\Big[\cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}+\vec{b}) + \cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}-\vec{b})\Big] \pm e_{10}\Big[\cos \vec{k}\cdot(\tfrac{1}{2}\{\vec{a}+\vec{b}\}+\vec{c}) + \\
& \cos \vec{k}(\tfrac{1}{2}\{\vec{a}-\vec{b}\}+\vec{c})\Big] \pm e_{11}\Big[\cos \vec{k}\cdot(\vec{c}+\tfrac{1}{2}\{\vec{b}-\vec{a}\}) + \\
& \cos \vec{k}\cdot(\vec{c}-\tfrac{1}{2}\{\vec{a}+\vec{b}\})\Big] + e_{12} \cos \vec{k}\cdot(\vec{c}-\vec{a}) + e_{13}\Big[\cos \vec{k}\cdot(\vec{c}-\vec{a}+\vec{b}) + \\
& \cos \vec{k}\cdot(\vec{c}-\vec{a}-\vec{b})\Big] \pm e_{14}\Big[\cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}+3\vec{b}) + \cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}-3\vec{b})\Big]\Big\}
\end{aligned} \tag{38}$$

where the 13 e_l's are the resonance integrals between molecule 1 at the origin and molecule l, as given by e_l in equation (21). To express the energy to first and second order, e_l is given by $e_l^o + e_l' + |e_l''|^2/\Delta e$ as given in equation (21), (34), and (37) respectively. In practice the field is placed in the x ($= \vec{a}$), y ($= \vec{b}$), and z ($= \vec{c}' = \vec{c} \sin\beta$, $\cos\beta = \vec{a}\cdot\vec{c}/|\vec{a}\cdot\vec{c}|$) directions, and the perturbed energy is calculated for each of these. If $\vec{k}$ is taken to be parallel to a reciprocal lattice vector $\vec{a}^{-1}$, $\vec{b}^{-1}$, or $\vec{c}^{-1}$,

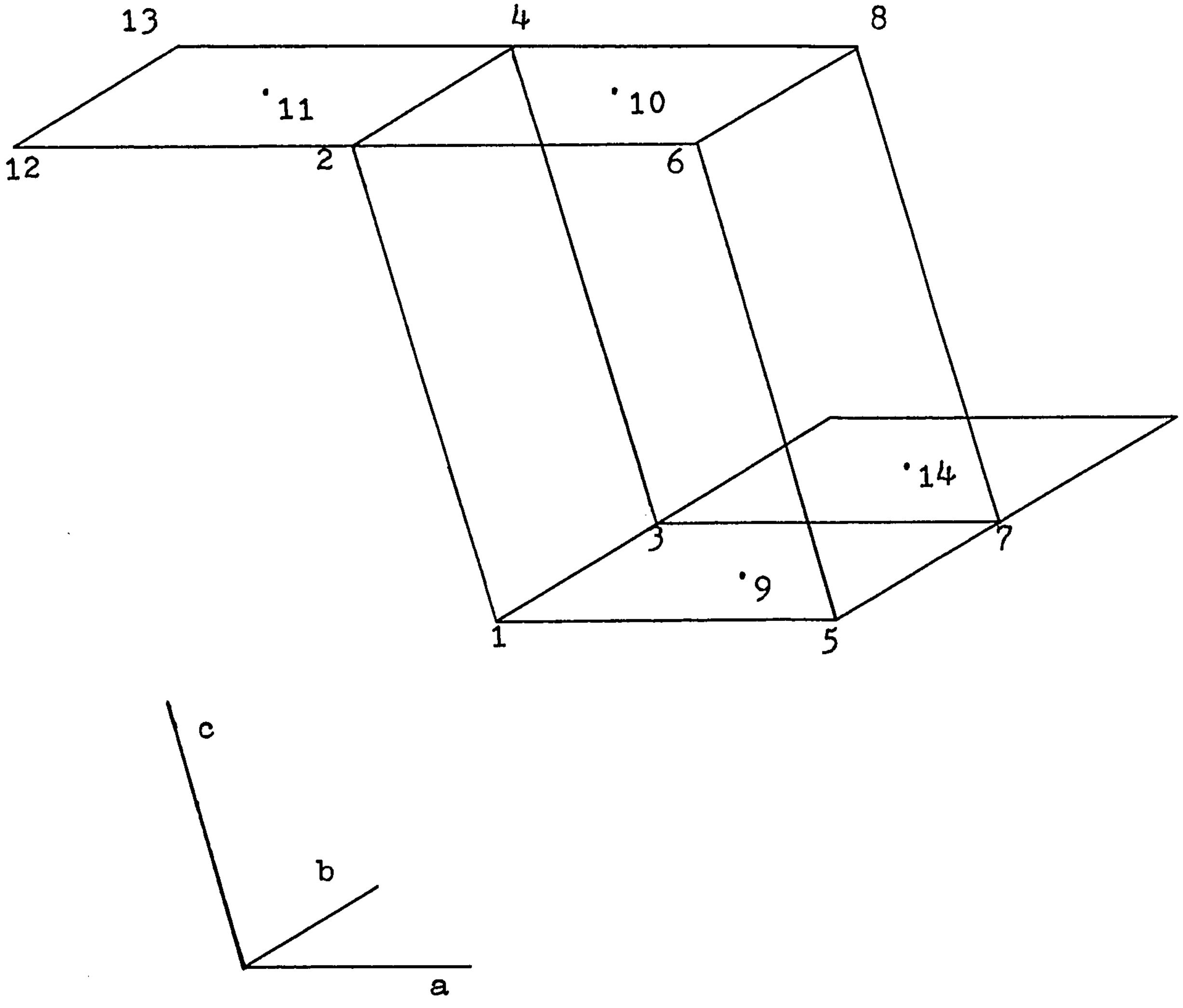


Figure 2. Schematic representation of the unit cell of anthracene or naphthalene, giving the numbering of the molecules used herein. (After ref. 37)

the energy can be readily plotted as a function of $\vec{k}$.

B. Numerical Calculations

In the tight-binding approximation of band theory, the electron band of anthracene is made up of a linear combination of the excess electron orbitals of the anthracene molecule while the hole band is constructed from the excess hole orbitals (cf. p. 8). Balk et al.(45) showed that the orbital occupied by the excess electron in an isolated negative aromatic ion can be expressed by using the Hückel coefficients which describe the first unoccupied orbital of the neutral molecule. So the molecular function $\phi(\vec{r})$ can be represented by the molecular orbital containing an extra electron or hole by using the LCAO method with Hückel(29) coefficients neglecting overlap:

$$\phi_n(\vec{r}) = \sum_i C_{in} u_i \qquad (39)$$

where the C_{in} are the Hückel coefficients of the n^{th} orbital and the $u_i(\vec{r})$ are the neutral carbon $2p_z$ atomic orbitals. The carbon atomic wave functions used were linear combinations of four Slater wave functions with coefficients a_i and orbital exponents α_i given by Clementi and Roothaan:(46)

$$u_i(\vec{r}) = (\hat{n}_i \cdot \vec{r}) \sum_{i=1}^{4} a_i (\alpha_i^5/\pi)^{1/2} \exp(-\alpha_i r) \qquad (40)$$

with $\hat{n}_i$ being the unit vector in the direction of the $2p_z$.

orbital. KRCJ also used this wave function because it gives the best fit to the tail of the wave function at the large distances which occur in the evaluation of the resonance and overlap integrals of molecules in crystals.

The integral e_1' is given by

$$e_1' = \sum_i \sum_j C_{in}C_{jn} \langle u_i(\vec{r}) \,|-e\vec{F}\cdot\vec{r}|\, u_j(\vec{r} - \vec{r}_1)\rangle \; . \quad (41)$$

When $\vec{F} = F_x\hat{i}$, or $F_y\hat{j}$, or $F_z\hat{k}$

$$e_1'(\gamma) = -eF_\gamma \sum_i \sum_j C_{in}C_{jn} \langle u_i(\vec{r})|\, r_\gamma |\, u_j(\vec{r} - \vec{r}_1)\rangle \quad (42)$$

where γ = x, y, or z and n is either the seventh or the eighth molecular orbital of anthracene.

For two identical nuclei,$^{(47)}$ R, the center of gravity between the two, is given by

$$R = \frac{\vec{r}_i + \vec{r}_j}{2} \quad (43)$$

where $\vec{r}_i$ and $\vec{r}_j$ are the vectors to atoms i and j, respectively. Also, since

$$R = \frac{\langle u_i | \vec{r} | u_j\rangle}{\langle u_i | u_j\rangle} = \frac{\langle u_i | \vec{r} | u_j\rangle}{S_{ij}} \; , \quad (44)$$

$$\langle u_i | \vec{r} | u_j\rangle = \frac{\vec{r}_i + \vec{r}_j}{2} \; S_{ij} , \quad (45)$$

and $$e_1' = -e\vec{F}\cdot\sum_i \sum_j C_{in}C_{jn} \frac{\vec{r}_i + \vec{r}_j + \vec{r}_1}{2} S_{ij}, \tag{46}$$

where now $\vec{r}_j + \vec{r}_1$ has been written for $\vec{r}_j$; $\vec{r}_1$ is the vector to the center of molecule 1 and $\vec{r}_j$ is the vector from the center of the molecule to atom j. The evaluation of S_{ij}, the overlap integral between the two wave functions, was performed by expanding the integral in the form (KRCJ):

$$S_{ij} = -\pi^{-1} \frac{(\hat{n}_i\cdot\vec{R}_{ij})(\hat{n}_j\cdot\vec{R}_{ij})}{R_{ij}^2} A_{ij} + (2\pi)^{-1} \times$$

$$\left[(\hat{n}_i\cdot\hat{n}_j) - \frac{(\hat{n}_i\cdot\vec{R}_{ij})(\hat{n}_j\cdot\vec{R}_{ij})}{R_{ij}^2}\right] B_{ij} \tag{47}$$

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

$$A_{ij} = \int r_i r_j \cos\gamma_i \cos\gamma_j \left[\sum_l a_l \alpha_l^{5/2} \exp(-\alpha_l r_i)\right] \times$$

$$\left[\sum_m a_m \alpha_m^{5/2} \exp(-\alpha_m r_j)\right] d\tau \tag{48}$$

$$B_{ij} = \int r_i r_j \mathrm{Sin}\gamma_i \mathrm{Sin}\gamma_j \left[\sum_l a_l \alpha_l^{5/2} \exp(-\alpha_l r_i)\right] \times$$

$$\left[\sum_m a_m \alpha_m^{5/2} \exp(-\alpha_m r_j)\right] d\tau \; ; \tag{49}$$

γ_i and γ_j are the angles which $\vec{r}_i$ and $\vec{r}_j$ make with $\vec{R}_{ij}$, respectively. Both A_{ij} and B_{ij} can be evaluated analytically in confocal elliptical coordinates (see Appendix I for details of the calculation), but since the result is a sum of many terms and there are 13 x 14 x 14 such integrals to be evaluated, an IBM 360/50 computer was used to compute the results. The program of this calculation is included in Appendix II.

The second order calculation of the perturbing field requires calculation of the integrals (cf. equation (37)):

$$e_1'' = \sum_i \sum_j c_{in} c_{jm} \left\langle u_i(\vec{r}) \mid -e\vec{F}\cdot\vec{r} \mid u_j(\vec{r}-\vec{r}_1) \right\rangle \qquad (50)$$

or
$$e_1''(\gamma) = -eF_\gamma \sum_i \sum_j c_{in} c_{jm} \left\langle u_i(\vec{r}) \mid r_\gamma \mid u_j(\vec{r}-\vec{r}_1) \right\rangle \qquad (51)$$

where γ = x, y, or z, n = 7 or 8 depending upon whether the hole band or the electron band is being calculated, and m is the number of the orbital from which or to which the electron or hole is being excited. The energy difference (cf. equation (36))

$$\Delta e = | e_m - e_n | \quad , \qquad (52)$$

is simply the energy difference between orbital m minus orbital n, found by using a value of 2.36 eV$^{(48)}$ for the atomic resonance integral. The allowed orbitals are determined such that the representation of the integral will be A_g, the total symmetric representation for the molecule which belongs to symmetry group D_{2h}. This requires the product of the representation of orbitals n and m to be either B_{1u} for a transition in the z (short axis) direction, or B_{2u} for a transition in the y (long axis) direction. There is no allowed molecular transition in the x direction. The allowed transitions in the crystal(49) will be given by the sums and differences of the molecular transitions for molecules of different orientation. The sum will belong to the B_u representation of the factor group C_{2h} of the crystal and will lie in the ac plane, while the difference has A_u symmetry and lies in the b direction.

C. Numerical Results

The crystal constants and fractional atomic coordinates for anthracene(50, 51) and naphthalene(52) are given in Table I. The fractional atomic coordinates have been referred to the orthogonal coordinate system used in the calculations (cf. p. 22) and have been converted to atomic units. Table II lists the intermolecular overlap integrals between molecule one and molecules two through fourteen calculated according to the method used by KRCJ using SCF functions.

The energy values calculated are tabulated in Table III. The perturbed energies were calculated for a field of 10^4 volts/cm and 10^5 volts/cm. As it turned out, the second order correction to the energy was negligible so that the perturbation was linear with the field.

Table I. Crystal constants and atomic coordinates of anthracene[50,51] and naphthalene.[52]

	a	b	c	
Anthracene	8.561 Å	6.036 Å	11.162 Å	$124^\circ 42'$
Naphthalene	8.235 Å	6.003 Å	8.658 Å	$122^\circ 55'$

	Anthracene (at. units)			Naphthalene (at. units)		
Atom no.*	x**	y	z**	x**	y	z**
1	1.5666	1.4927	-1.5581	0.4224	1.1628	0.4821
2	3.1706	2.9503	-3.1627	1.8627	2.8031	-1.0768
3	3.8619	2.0444	-5.4824	2.4399	2.1203	-3.4900
4	2.9773	-0.3315	-6.3451	1.5585	-0.2111	-4.4651
5	1.4466	-1.7735	-4.8663	0.1695	-1.8015	-3.0217
6	0.7043	-0.9368	-2.3962	-0.4224	-1.1628	-0.4821
7	-1.5666	-1.4927	1.5581	-1.8627	-2.8031	1.0768
8	-3.1706	-2.9503	3.1627	2.4399	-2.1203	3.4900
9	-3.8619	-2.0444	5.4824	-1.5585	0.2111	4.4651
10	-2.9773	0.3315	6.3451	-0.1695	1.8015	3.0217
11	-1.4466	1.7735	4.8663			
12	-0.7043	0.9368	2.3962			
13	0.8466	2.3779	-0.8200			
14	-0.8466	-2.3779	0.8200			

Normal to the plane

n_x	n_y	n_z	n_x	n_y	n_z
0.8059	-0.4347	0.4020	0.8399	-0.4425	0.3143

* The numbering follows that given in Figure 1, p. 16 for anthracene; naphthalene is analogous.

** $x = a + c \cos\beta$; $z = c \sin\beta$

Table II. Overlap integrals for anthracene calculated from SCF functions in units of 10^{-4} eV.

Molecule Number	Hole	Electron
2	0.77	0.99
3	54.85	-27.24
4	0.28	0.04
5	-0.28	-0.24
6	3.49	0.60
7	-0.07	-0.04
8	0.03	-0.02
9	35.81	40.83
10	-16.93	-1.62
11	-0.02	-0.03
12	0.00	0.00
13	0.00	0.00
14	-0.02	-0.01

Table III. Intermolecular resonance integrals for anthracene perturbed by an electric field of 10^5 volts/cm applied in the x, y, and z directions in units of 10^{-4}eV.

Molecule number	e_1(KRCJ)	e_1' (x)	e_1' (y)	e_1' (z)
		Hole		
2	-0.47	0.003	0.000	-0.005
3	-132.44	0.000	-0.234	0.000
4	-0.17	0.001	-0.001	-0.002
5	0.20	0.002	0.000	0.000
6	-4.39	-0.005	0.000	-0.023
7	0.03	0.000	0.000	0.000
8	-0.03	0.000	0.000	0.000
9	-93.05	-0.137	-0.090	-0.017
10	36.61	-0.018	0.037	0.114
11	0.01	0.000	0.000	0.000
12	0.00	0.000	0.000	0.000
13	0.00	0.000	0.000	0.000
14	0.01	0.000	0.000	0.000
$E_+(k = 0)$	-500.56	0.001	0.469	0.055
$E_-(k = 0)$	-49.20	1.243	0.889	-0.725
		Electron		
2	0.15	0.004	0.000	-0.006
3	71.61	0.000	0.116	0.000
4	-0.03	0.000	0.000	0.000
5	0.25	0.001	0.000	0.000
6	-0.74	-0.001	0.000	-0.004
7	0.04	0.000	0.000	0.000
8	0.02	0.000	0.000	0.000
9	-124.79	-0.147	-0.095	-0.026
10	2.48	-0.003	0.003	0.010
11	0.02	0.000	0.000	0.000
12	0.00	0.000	0.000	0.000
13	0.00	0.000	0.000	0.000
14	0.00	0.000	0.000	0.000
$E_+(k = 0)$	-346.50	-0.588	-0.135	-0.085
$E_-(k = 0)$	631.82	0.611	0.600	0.043

Therefore, only the energy of interaction between molecule one and molecules two through fourteen for an applied field in the x, y, and z directions, along with the unperturbed energies calculated by KRCJ are given. In addition, E_+ and E_- (cf. equation (38)) are given for the case $\vec{k} = 0$.

As is expected, the effect of the applied field is very slight, so that the energy bands as plotted in KRCJ are changed very little. The same is also true of the mobilities calculated by KRCJ.

III. SURFACE STATES OF ANTHRACENE AND NAPHTHALENE.

Generally, when studying the electronic structure of a crystal, only those aspects independent of the conditions existing at a free surface or interface are considered. The purpose of this study, however, has been to supplement the energy band structures of anthracene and naphthalene, previously calculated by Katz, Rice, Choi, and Jortner (KRCJ)(37) with a calculation of their surface bands using a crystal orbital approach.(39, 40)

A. Method of Calculation

Both anthracene and naphthalene have a monoclinic structure with two molecules per unit cell (cf. Fig. 1, p.16). The two molecules of the unit cell are differently oriented, and will result in two energy bands for each electronic state, corresponding to the symmetric and antisymmetric combinations of the wave functions of the molecules in the unit cell. These energy bands have been calculated by KRCJ, using the tight-binding approximation, since the binding energy of the molecular crystal is very small relative to the excitation energy of the excited electronic states of the molecule.

The one electron crystal wave functions are constructed as Bloch sums(27) of the one electron molecular wave function, $\phi(\vec{r} - \vec{r}_m)$:

$$\Psi_{\pm}(k) = \sum_{m_1}\sum_{m_2}\sum_{m_3} (\pm 1)^m \phi(\vec{r} - \vec{r}_m)\, C(\vec{k},\vec{r}_m), \tag{53}$$

where $\vec{r}_m$ represents the vector from the origin to the center of the molecule with coordinates $(m_1\vec{a}, m_2\vec{b}, m_3\vec{c})$, $\vec{a}$, $\vec{b}$, and $\vec{c}$, being the three crystallographic axes (cf. Fig. 1, p. 16), $\vec{k}$ is the wave vector, and

$$C(\vec{k}, \vec{r}_m) = \sin \vec{k}\cdot(\vec{r}_N - \vec{r}_{m2}) \sin \vec{k}\cdot(\vec{r}_{m1} + \vec{r}_{m3}) \tag{54a}$$

or,

$$C(\vec{k}, \vec{r}_m) = \sin \vec{k}\cdot(\vec{r}_N - \vec{r}_{m1} - \vec{r}_{m3}) \sin \vec{k}\cdot\vec{r}_{m2} \tag{54b}$$

$\Psi_{+}(\vec{k})$ is the symmetric wave function and gives an energy $E_{+}(\vec{k})$, while $\Psi_{-}(\vec{k})$, the antisymmetric wave function, gives an energy $E_{-}(\vec{k})$. To calculate the surface band for an excess electron or hole, the following Hamiltonian is used (cf. KRCJ and p. 17):

$$H = (-\hbar^2/2m)\nabla^2 + V(\vec{r}), \tag{55}$$

where

$$V(\vec{r}) = V_n(\vec{r} - \vec{r}_n) \tag{56}$$

V_n being the Hartree potential of an isolated neutral molecule. By following the formulation and using the approximations described in Chapter II and in KRCJ, one obtains for the energy the expression

$$E_{\pm}(\vec{k}) = \alpha + \sum_{l} (\pm 1)^l e_l \cos \vec{k}\cdot\vec{r}_l, \tag{57}$$

where

$$\alpha = e_0 + \sum_{n}{}' e_n \tag{58}$$

and

$$e_o = \langle \phi \mid H^o \mid \phi \rangle , \tag{59}$$

$$H^o = (-\hbar^2/2m)\nabla^2 + V_n, \tag{60}$$

$$e_n = \langle \phi \mid V_n(\vec{r} - \vec{r}_n) \mid \phi \rangle , \tag{61}$$

$$e_l = \langle \phi(\vec{r} - \vec{r}_l) \mid V(\vec{r} - \vec{r}_l) \mid \phi(\vec{r}) \rangle , \tag{62}$$

and the sums are taken over all molecules except the one with its center located at the origin. By convention, l even refers to a molecule at the corner of the unit cell, while l odd refers to a molecule at the center of the unit cell. Unlike the Born-von Kármán boundary conditions used for calculating the bulk energy bands of crystals, the boundary condition for the surface requires(40) that

$$\left[E\pm(\vec{k}) - \alpha'\right] C(\vec{k},\vec{r}_o,\vec{r}_{12},\vec{r}_{13}) = \sum_l (\pm 1)^l e_l \left[C(\vec{k},\vec{r}_1,\vec{r}_{12},\vec{r}_{13}) + C(\vec{k},\vec{r}_o,\vec{r}_{12\pm 1},\vec{r}_{13\pm 1})\right] \tag{63}$$

where $\vec{r}_o$ and $\vec{r}_1$ are components of the vector perpendicular to the surface, while $\vec{r}_{12\pm 1}$ and $\vec{r}_{13\pm 1}$ represent the other two components of $\vec{r}_1$, and

$$\alpha' = e_o' + \sum{}' e_n'. \tag{64}$$

e_o' is the energy of an isolated negative ion on the surface and e_n' and e_l' are the resonance integrals between the surface molecule with its center at the origin and the molecule in position n (equation (61)) or l (equation (62)), respectively. Because of the symmetry of the crystal, each coefficient with a term $\vec{r}_{12+1}$ or $\vec{r}_{13+1}$ is paired with one containing a term $\vec{r}_{12-1}$ or $\vec{r}_{13-1}$ so that the sum of the two results in a cosine term; because of the surface, this symmetry does not exist in direction $\vec{r}_{11}$ and a term in $\vec{k}\cdot\vec{r}_{11}$ with real and imaginary solutions appears.

In order to solve this problem for a particular surface of the crystal, the integrals e_n and e_1 are calculated only for the interaction between molecule number one and molecules numbered two through fourteen in Fig. 2 (p.23). Then, the nearest neglected molecule has no atoms closer than 7.5 Å. For the purposes of this study, the integrals e_n' and e_1' (for which the origin is taken to be on the surface), have been assumed to be approximately equal to the integrals e_n and e_1, respectively (for which the origin is taken to be within the crystal). This, in effect, assumes that the atomic coordinates of the surface molecules are the same as those within the crystal, which is a reasonable assumption in light of the other approximations made herein. The integrals e_1 have been calculated in KRCJ including all three center integrals between the potential and wave functions on neighboring atoms with the wave functions on another molecule. In order to calculate the surface states, the integrals e_n had to be calculated, and all three center integrals between two wave functions on nearest-neighbor (NN), next-nearest neighbor (NNN), and next-next-nearest-neighbor (NNNN) atoms with the potential on a second molecule were included.

The energy of the crystal is given by (cf. KRCJ and equation (38), p. 22):

$$E_{\pm}(\vec{k}) = e_o + 2(e_{n2} + e_{n3} + 2e_{n4} + e_{n5} + e_{n6} + 2e_{n7} + 2e_{n8} + 2e_{n9} + 2e_{n10} + 2e_{n11} + e_{n12} + 2e_{n13} + 2e_{n14}) + 2\left\{e_2 \cos \vec{k}\cdot\vec{c} + e_3 \cos \vec{k}\cdot\vec{b} + e_4\left[\cos \vec{k}\cdot(\vec{b}+\vec{c}) + \cos \vec{k}\cdot(\vec{b}-\vec{c})\right] + e_5 \cos \vec{k}\cdot\vec{a} + e_6 \cos \vec{k}\cdot(\vec{a}+\vec{c}) + e_7\left[\cos \vec{k}\cdot(\vec{a}+\vec{b}) + \cos \vec{k}\cdot(\vec{a}-\vec{b})\right] + e_8\left[\cos \vec{k}\cdot(\vec{a}+\vec{b}+\vec{c}) + \cos \vec{k}\cdot(\vec{a}-\vec{b}+\vec{c})\right] \pm e_9\left[\cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}+\vec{b}) + \cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}-\vec{b})\right] \pm e_{10}\left[\cos \vec{k}\cdot(\tfrac{1}{2}\{\vec{a}+\vec{b}\}+\vec{c}) + \cos \vec{k}\cdot(\tfrac{1}{2}\{\vec{a}-\vec{b}\}+\vec{c})\right] \pm e_{11}\left[\cos \vec{k}\cdot(\tfrac{1}{2}\{\vec{a}+\vec{b}\}-\vec{c}) + \cos \vec{k}\cdot(\tfrac{1}{2}\{\vec{a}-\vec{b}\}-\vec{c})\right] + e_{12} \cos \vec{k}\cdot(\vec{a}-\vec{c}) + e_{13}\left[\cos \vec{k}\cdot(\vec{a}+\vec{b}-\vec{c}) + \cos \vec{k}\cdot(\vec{a}-\vec{b}-\vec{c})\right] \pm e_{14}\left[\cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}+3\vec{b}) + \cos \vec{k}\cdot\tfrac{1}{2}(\vec{a}-3\vec{b})\right]\right. . \tag{65}$$

Applying the boundary conditions (equation (63)) for a surface in the <u>ac</u> plane one obtains:

$$E_{\pm}(\vec{k}) = e'_o + e'_{n3} + 2(e'_{n2} + e'_{n4} + e'_{n5} + e'_{n6} + e'_{n7} + e'_{n8} + e'_{n9} + e'_{n10} + e'_{n11} + e'_{n12} + e'_{n13} + e'_{n14}) + (\cos \vec{k}\cdot\vec{b} - \sin \vec{k}\cdot\vec{b} \cot \vec{k}\cdot N\vec{b})\ x \left[e_3 + 2e_4 \cos \vec{k}\cdot\vec{c} + 2e_7 \cos \vec{k}\cdot\vec{a} + 2e_8 \cos \vec{k}\cdot(\vec{a}+\vec{c}) + 2e_{13} \cos \vec{k}\cdot(\vec{a}-\vec{c})\right] \pm 2(\cos \vec{k}\cdot\vec{b}/2 - \sin \vec{k}\cdot\vec{b}/2 \cot \vec{k}\cdot N\vec{b}/2)\left[e_9 \cos \vec{k}\cdot\vec{a}/2 + e_{10} \cos \vec{k}\cdot(\vec{a}/2 + \vec{c}) + e_{11} \cos \vec{k}\cdot(\vec{a}/2 - \vec{c})\right] \pm 2(\cos \vec{k}\cdot 3\vec{b}/2 - \sin \vec{k}\cdot 3\vec{b}/2 \cot \vec{k}\cdot 3N\vec{b}/2)\ x\ e_{14} \cos \vec{k}\cdot\vec{a}/2 + 2\left[e_2 \cos \vec{k}\cdot\vec{c} + e_5 \cos \vec{k}\cdot\vec{a} + e_6 \cos \vec{k}\cdot(\vec{a}+\vec{c}) + e_{12} \cos \vec{k}\cdot(\vec{a}-\vec{c})\right] . \tag{66}$$

By subtracting equation (66) from equation (65) one obtains:

$$\alpha - \alpha' + (\cos \vec{k}\cdot\vec{b} + \sin \vec{k}\cdot\vec{b} \cot \vec{k}\cdot N\vec{b}) \Big[e_3 + 2e_4 \cos \vec{k}\cdot\vec{c} + 2e_7 \cos \vec{k}\cdot\vec{a} + 2e_8 \cos \vec{k}\cdot(\vec{a} + \vec{c}) + 2e_{13} \cos \vec{k}\cdot(\vec{a} - \vec{c})\Big] \pm 2(\cos \vec{k}\cdot\vec{b}/2 + \sin \vec{k}\cdot\vec{b}/2 \cot \vec{k}\cdot N\vec{b}/2)\Big[e_9 \cos \vec{k}\cdot\vec{a}/2 + e_{10} \cos \vec{k}\cdot(\vec{a}/2 + \vec{c}) + e_{11} \cos \vec{k}\cdot(\vec{a}/2 - \vec{c})\Big] \pm 2(\cos \vec{k}\cdot 3\vec{b}/2 + \sin \vec{k}\cdot 3\vec{b}/2 \cot \vec{k}\cdot 3N\vec{b}/2) \times e_{14} \cos \vec{k}\cdot\vec{a}/2 = 0. \tag{67}$$

where,

$$\alpha - \alpha' = e_{n3} + 2(e_{n4} + e_{n7} + e_{n8} + e_{n9} + e_{n10} + e_{n11} + e_{n13} + e_{n14}), \tag{68}$$

the approximation being the equating of e_n and e_n' as mentioned above. No serious error is made by ignoring molecule number 14 in equations (67) and (68) since it contributes less than 0.1% to the energy, and by doing this an unwieldy cubic equation is reduced to a quadratic equation. A surface band will be present if $\vec{k}\cdot\vec{b}$ is of the form $\mu + i\xi$ where ξ and μ are real and positive.(39) ξ must be positive to insure the exponential decay of the wave function into the crystal. A necessary condition for the energy to remain real is that $\text{Im} \cos \vec{k}\cdot\vec{b} = \text{Im} \cos \vec{k}\cdot\vec{b}/2 = 0$, thus

$$\sin \mu \sinh \xi = \sin \mu/2 \sinh \xi/2 = 0 \tag{69}$$

which means that μ must be equal to $2n\pi (n = 0,1,2\ldots)$, but only the case $n = 0$ need be considered, since all other values of n are equivalent to this. This is obvious for the case of $n > 1$. The case of $n = 1$ is discussed below.

Substitution into equation (67) of $\vec{k}\cdot\vec{b} = i\xi$ gives terms of the form

$$\cosh\xi + \sinh\xi \coth N\xi \tag{70a}$$

$$\cosh \xi/2 + \sinh\xi/2 \coth N\xi/2. \tag{70b}$$

These reduce to exp (ξ) and exp ($\xi/2$) for very large N, so that equation (67) becomes a quadratic in exp ($\xi/2$). A convenient way to plot the surface bands of anthracene and naphthalene is to plot $E\pm(\vec{k})$ for $\vec{k}$ parallel to each of the three reciprocal lattice vectors, $\vec{a}^{-1}$, $\vec{b}^{-1}$, and $\vec{c}^{-1}$, respectively. Then:

$$E\pm(\vec{k}\,||\,\vec{a}^{-1}) = \alpha + \left[2A_1\cosh(\xi_1) \pm 4B_1\cosh(\xi_1/2) + D_1\right] \tag{71a}$$

$$E\pm(\vec{k}\,||\,\vec{b}^{-1}) = \alpha + \left[2A_2\cosh(\xi_2) \pm 4B_2\cosh(\xi_2/2) + D_2\right] \tag{71b}$$

$$E\pm(\vec{k}\,||\,\vec{c}^{-1}) = \alpha + \left[2A_3\cosh(\xi_3) \pm 4B_3\cosh(\xi_3/2) + D_3\right] \tag{71c}$$

$$A_1(\vec{k}\,||\,\vec{a}^{-1}) = e_3 + 2e_4 + 2(e_7 + e_8 + e_{13}) \cos \vec{k}\cdot\vec{a}$$

$$A_2(\vec{k}\,||\,\vec{b}^{-1}) = e_3 + 2(e_4 + e_7 + e_8 + e_{13})$$

$$A_3(\vec{k}\,||\,\vec{c}^{-1}) = e_3 + e_7 + 2(e_4 + e_8 + e_{13})\cos \vec{k}\cdot\vec{c}$$

$$B_1(\vec{k}\,||\,\vec{a}^{-1}) = (e_9 + e_{10} + e_{11}) \cos \vec{k}\cdot\vec{a}/2$$

$$B_2(\vec{k}\,||\,\vec{b}^{-1}) = e_9 + e_{10} + e_{11}$$

$$B_3(\vec{k}\,||\,\vec{c}^{-1}) = e_9 + (e_{10} + e_{11}) \cos \vec{k}\cdot\vec{c}$$

$C = \alpha - \alpha'$ (cf. equation (68))

$$D_1(\vec{k}\,||\,\vec{a}^{-1}) = 2e_2 + 2(e_5 + e_6 + e_{12}) \cos \vec{k}\cdot\vec{a}$$

$$D_2(\vec{k}\,||\,\vec{b}^{-1}) = 2(e_2 + e_5 + e_6 + e_{12})$$

$$D_3(\vec{k}\ \ \vec{c}^{-1}) = 2e_5 + 2(e_2 + e_6 + e_{12})\cos \vec{k}\cdot\vec{c} \tag{72}$$

$$P_+ \equiv e^{\xi_i/2} = (-B_i \pm\sqrt{B_i^2 - A_iC})/A_i;\ \xi_i = 2 \ln P_+ \tag{73a}$$

$$P_- \equiv e^{\xi_i/2} = (+B_i \pm\sqrt{B_i^2 - A_iC})/A_i;\ \xi_i = 2 \ln P_- \tag{73b}$$

where $\xi = -i\vec{k}\cdot\vec{b}$ and $i = 1,2,3$. If $\exp(\xi_i/2)$ is positive, it is labeled P_+ or P_- depending upon whether the value refers to the symmetric or antisymmetric energy band, respectively. If $\exp(\xi_i/2)$ is negative, it is labeled N_+ or N_-.

A surface band exists for values of P_+ or P_- real and greater than unity since ξ is greater than zero. If one of the P_+ roots is real and positive and the other real and negative, the negative root will have an equivalent positive value in one of the two possible P_- roots (one of which will be negative and have the absolute value of the positive P_+ root), resulting in two surface bands. Alternatively, a negative value for $e^{\xi/2}$ could be resolved by taking $\vec{k}\cdot\vec{b} = 2\pi + i\xi$ and calling this an N_+ root. But substitution of $2\pi + i\xi$ into the energy equation for $\vec{k}\cdot\vec{b}$ will give the same value for the energy as the P_- root. There are, therefore, only two non-equivalent bands. It can also be shown (as pointed out in KRCJ), that the apparent periodicity of $4\pi\vec{a}^{-1}$ in equation (71a) is only $2\pi\vec{a}^{-1}$ since

$$\Psi_+(\vec{k} + 2\pi\vec{a}^{-1}) = \Psi_-(\vec{k}) \tag{74a}$$

$$\Psi_-(\vec{k} + 2\pi\vec{a}^{-1}) = \Psi_+(\vec{k}) \tag{74b}$$

The same relations will hold below for surfaces in the <u>ab</u> or <u>bc</u> plane for $\vec{k} \| \vec{b}^{-1}$.

Applying the boundary conditions for a surface in the <u>ab</u> plane results in:

$$\begin{aligned}
E\pm(\vec{k}) ={}& e_o' + 2(e_{n3}' + e_{n5}' + 2e_{n7}' + 2e_{n9}' + 2e_{n14}') + (e_2 + 2e_4 \cos \vec{k}\cdot\vec{b}) \times \\
& \left[\cos \vec{k}\cdot\vec{c} - \sin \vec{k}\cdot\vec{c} \cot \vec{k}\cdot(N\vec{c} - m_1\vec{a})\right] + (e_6 + 2e_8 \cos \vec{k}\cdot\vec{b})\Big\{\cos \vec{k}\cdot(\vec{c}+ \\
& \vec{a}) - \sin \vec{k}\cdot(\vec{c}+\vec{a})\cot \vec{k}\cdot\left[N\vec{c} - (m_1+1)\vec{a}\right]\Big\} + (e_{12} + 2e_{13}\cos \vec{k}\cdot\vec{b})\Big\{\cos \vec{k}\cdot(\vec{c}- \\
& \vec{a}) - \sin \vec{k}\cdot(\vec{c}-\vec{a})\cot \vec{k}\cdot\left[N\vec{c} - (m_1-1)\vec{a}\right]\Big\} \pm 2e_{10}\cos \vec{k}\cdot\vec{b}/2\Big\{\cos \vec{k}\cdot(\vec{c}+ \\
& \vec{a}/2) - \sin \vec{k}\cdot(\vec{c}+\vec{a}/2)\cot \vec{k}\cdot\left[N\vec{c} - (m_1+\tfrac{1}{2})\vec{a}\right]\Big\} \pm 2e_{11}\cos \vec{k}\cdot\vec{b}/2\Big\{\cos \vec{k}\cdot(\vec{c}- \\
& \vec{a}/2) - \sin \vec{k}\cdot(\vec{c}-\vec{a}/2)\cot \vec{k}\cdot\left[N\vec{c} - (m_1-\tfrac{1}{2})\vec{a}\right]\Big\} + 2\Big[e_3\cos \vec{k}\cdot\vec{b} + e_5\cos \vec{k}\cdot\vec{a} + \\
& 2e_7\cos \vec{k}\cdot a \cos \vec{k}\cdot\vec{b} \pm 2(e_9\cos \vec{k}\cdot\vec{a}/2 \cos \vec{k}\cdot\vec{b}/2 + \\
& e_{14}\cos \vec{k}\cdot\vec{a}/2 \cos \vec{k}\cdot 3\vec{b}/2)\Big] \;.
\end{aligned} \tag{75}$$

Subtracting equation (75) from equation (65) gives:

$$\begin{aligned}
& \alpha - \alpha' + (e_2 + 2e_4 \cos \vec{k}\cdot\vec{b})\left[\cos \vec{k}\cdot\vec{c} + \sin \vec{k}\cdot\vec{c} \cot \vec{k}\cdot(N\vec{c}-m_1\vec{a})\right] + \\
& (e_6 + 2e_8\cos \vec{k}\cdot\vec{b})\Big\{\cos \vec{k}\cdot(\vec{c}+\vec{a}) + \sin \vec{k}\cdot(\vec{c}+\vec{a}) \cot \vec{k}\cdot\left[N\vec{c}-(m_1+1)\vec{a}\right]\Big\} + \\
& (e_{12} + 2e_{13}\cos \vec{k}\cdot\vec{b})\Big\{\cos \vec{k}\cdot(\vec{c}-\vec{a}) + \sin \vec{k}\cdot(\vec{c}-\vec{a})\cot \vec{k}\cdot\left[N\vec{c}-(m_1-1)\vec{a}\right]\Big\} \pm \\
& 2e_{10}\cos \vec{k}\cdot\vec{b}/2\Big\{\cos \vec{k}\cdot(\vec{c}+\vec{a}/2) + \sin \vec{k}\cdot(\vec{c}+\vec{a}/2)\cot \vec{k}\cdot\left[N\vec{c}-(m_1+\tfrac{1}{2})\vec{a}\right]\Big\} \pm \\
& 2e_{11}\cos \vec{k}\cdot\vec{b}/2\Big\{\cos \vec{k}\cdot(\vec{c}-\vec{a}/2) + \sin \vec{k}\cdot(\vec{c}-\vec{a}/2)\cot \vec{k}\cdot\Big[N\vec{c} - (m_1 - \\
& \tfrac{1}{2})\vec{a}\Big]\Big\} = 0,
\end{aligned} \tag{76}$$

where

$$\alpha - \alpha' = e_{n2} + e_{n6} + e_{n12} + 2(e_{n4} + e_{n8} + e_{n10} + e_{11} + e_{n13}) . \tag{77}$$

This equation results in a surface band if $\vec{k}\cdot\vec{c}$ is complex. In order for the energy to be real, two conditions must be met: first, for $\vec{k}\cdot\vec{c} = \mu + i\xi$, μ, ξ real > 0, μ must be equal to $n\pi (n = 0,1,\ldots)$, and second, $\vec{k}\cdot\vec{a}$ must be equal to $2n\pi (n = 0, 1,\ldots)$. As before, only the values n = 0 or 1 are unique for both cases. Under these conditions, equation (76) reduces to

$$\alpha - \alpha' + e^{\xi}\left[e_2 + 2e_4\cos \vec{k}\cdot\vec{b} + e_6 + e_{12} + 2(e_8+e_{13})\cos \vec{k}\cdot\vec{b}\right] \pm 2(e_{10} + e_{11}) \cos \vec{k}\cdot\vec{b}/2 = 0, \qquad (76a)$$

which is simply a linear equation in e^{ξ}.

The restriction on the values of $\vec{k}\cdot\vec{a}$ results in a surface state in the $\vec{k} \| \vec{a}^{-1}$ as well as the $\vec{k} \| \vec{c}^{-1}$ direction, and a surface band in the $\vec{k} \| \vec{b}^{-1}$ direction. The energies for these three cases then are

$$E\pm(\vec{k} \| \vec{a}^{-1}) = \alpha \pm 2(A_1 \pm B_1) \cosh \xi_1 + D_1 \pm 4(e_9+e_{14}) \qquad (78a)$$

$$E\pm(\vec{k} \| \vec{b}^{-1}) = \alpha \pm 2(A_2 \pm B_2) \cosh \xi_2 + D_2 \pm 4(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2) \qquad (78b)$$

$$E\pm(\vec{k} \| \vec{c}^{-1}) = \alpha \pm 2(A_3 \pm B_3) \cosh \xi_3 + D_3 \pm 4(e_9+e_{14}) \qquad (78c)$$

where,

$A_1(\vec{k} \| \vec{a}^{-1}) = A_3(\vec{k} \| \vec{c}^{-1}) = e_2 + e_6 + e_{12} + 2(e_4 + e_8 + e_{13})$.

since $\vec{k}\cdot\vec{a} = 0, 2$

$A_2(\vec{k} \| \vec{b}^{-1}) = e_2 + e_6 + e_{12} + 2(e_4 + e_8 + e_{13}) \cos \vec{k}\cdot\vec{b}$

$B_1(\vec{k} \| \vec{a}^{-1}) = B_3(\vec{k} \| \vec{c}^{-1}) = 2(e_{10} + e_{11})$

$B_2(\vec{k} \| \vec{b}^{-1}) = 2(e_{10} + e_{11}) \cos \vec{k}\cdot\vec{b}/2$

$$C = \alpha - \alpha' \text{ (cf. equation (77))}$$

$$D_1(\vec{k} \,||\, \vec{a}^{-1}) = D_3(\vec{k} \,||\, \vec{c}^{-1}) = 2(e_3 + e_5 + 2e_7)$$

$$D_2(\vec{k} \,||\, \vec{b}^{-1}) = 2e_5 + 2(e_3 + 2e_7)\cos \vec{k}\cdot\vec{b} \qquad (79)$$

and,

$$\exp(\xi_i) = -C/(A_i \pm B_i); \; i = 1,2,3. \qquad (80)$$

If either of the roots for e^{ξ} are >1 then $\mu = 0$ and a P_+ or P_- state exists. On the other hand, a value for $e^{\xi} < -1$ implies that $\mu = \pi$, and the states are called N_+ or N_-. A P or an N state results in a (+) or (−) value respectively for the first double sign notation on the right hand side of equation (78), while the sign of the subsequent double sign notations are determined by whether the band is (+) or (−).

Finally, applying the boundary condition to the

$$E\pm(\vec{k}) = \alpha' + (e_5 + 2e_7\cos \vec{k}\cdot\vec{b})\left[\cos \vec{k}\cdot\vec{a} - \sin \vec{k}\cdot\vec{a} \cot \vec{k}\cdot(N\vec{a}-m_3\vec{c})\right] +$$
$$(e_6 + 2e_8\cos \vec{k}\cdot\vec{b})\left\{\cos \vec{k}\cdot(\vec{a}+\vec{c}) - \sin \vec{k}\cdot(\vec{a}+\vec{c})\cot \vec{k}\cdot\left[N\vec{a}-(m_3+1)\vec{c}\right]\right\} +$$
$$(e_{12} + 2e_{13}\cos \vec{k}\cdot\vec{b})\left\{\cos \vec{k}\cdot(\vec{a}-\vec{c}) - \sin \vec{k}\cdot(\vec{a}-\vec{c})\cot \vec{k}\cdot\left[N\vec{a}-(m_3-1)\vec{c}\right]\right\} \pm$$

$$2(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2)\left[\cos \vec{k}\cdot\vec{a}/2 - \sin \vec{k}\cdot\vec{a}/2 \cot \vec{k}\cdot(N\vec{a}/2-\right.$$

$$2(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2)\left[\cos \vec{k}\cdot\vec{a}/2 - \sin \vec{k}\cdot\vec{a}/2 \cot \vec{k}\cdot(N\vec{a}/2-\right.$$
$$\left.m_3\vec{c})\right] \pm 2e_{10}\cos \vec{k}\cdot\vec{b}/2\left\{\cos \vec{k}\cdot(\vec{a}/2 + \vec{c}) - \sin \vec{k}\cdot(\vec{a}/2 + \vec{c}) \times\right.$$
$$\left.\cot \vec{k}\cdot\left[N\vec{a}/2 - (m_3+1)\vec{c}\right]\right\} \pm 2e_{11}\cos \vec{k}\cdot\vec{b}/2\left\{\cos \vec{k}\cdot(\vec{a}/2 - \vec{c}) -\right.$$
$$\left.\sin \vec{k}\cdot(\vec{a}/2 - \vec{c}) \cot \vec{k}\cdot\left[N\vec{a}/2 - (m_3-1)\vec{c}\right]\right\} + 2(e_2\cos \vec{k}\cdot\vec{c} +$$
$$e_3 \cos \vec{k}\cdot\vec{b} + 2e_4 \cos \vec{k}\cdot\vec{b} \cos \vec{k}\cdot\vec{c}), \qquad (81)$$

where

$$\alpha' = e_o' + 2(e_{n2}' + e_{n3}' + 2e_{n4}') + e_{n5}' + e_{n6}' + e_{n12}' + 2(e_{n7}' + e_{n8}' + e_{n9}' + e_{n10}' + e_{n11}' + e_{n13}' + e_{n14}'). \qquad (82)$$

Subtracting equation (81) from equation (65) yields:

$$\alpha - \alpha' + (e_5 + 2e_7\cos \vec{k}\cdot\vec{b})\left[\cos \vec{k}\cdot\vec{a} + \sin \vec{k}\cdot\vec{a} \cot \vec{k}\cdot(N\vec{a}-m_3\vec{c})\right] + (e_6 + 2e_8\cos \vec{k}\cdot\vec{b})\left\{\cos \vec{k}\cdot(\vec{a}+\vec{c}) + \sin \vec{k}\cdot(\vec{a}+\vec{c})\cot \vec{k}\cdot\left[N\vec{a}-(m_3+1)\vec{c}\right]\right\} + (e_{12} + 2e_{13}\cos \vec{k}\cdot\vec{b})\left\{\cos \vec{k}\cdot(\vec{a}-\vec{c}) + \sin \vec{k}\cdot(\vec{a}-\vec{c})\cot \vec{k}\cdot\left[N\vec{a}-(m_3-1)\vec{c}\right]\right\} \pm 2(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2)\left[\cos \vec{k}\cdot\vec{a}/2 + \sin \vec{k}\cdot\vec{a}/2 \cot \vec{k}\cdot(N\vec{a}-m_3\vec{c}\right] \pm 2e_{10}\cos \vec{k}\cdot\vec{b}/2\left\{\cos \vec{k}\cdot(\vec{a}/2+\vec{c}) + \sin \vec{k}\cdot(\vec{a}/2+\vec{c})\cot \vec{k}\cdot\left[N\vec{a}/2 - (m_3+1)\vec{c}\right]\right\} \pm 2e_{11}\cos \vec{k}\cdot\vec{b}/2\left\{\cos \vec{k}\cdot(\vec{a}/2-\vec{c}) + \sin \vec{k}\cdot(\vec{a}/2-\vec{c})\cot \vec{k}\cdot\left[N\vec{a}/2 - (m_3-1)\vec{c}\right]\right\} = 0 \qquad (83)$$

where

$$\alpha - \alpha' = e_{n5} + e_{n6} + e_{n12} + 2(e_{n7} + e_{n8} + e_{n9} + e_{n10} + e_{n11} + e_{n13} + e_{n14}). \qquad (84)$$

This equation results in a surface band for complex values of $\vec{k}\cdot\vec{a}$. Now, however, in order for the energy of the surface to remain real when $\vec{k}\cdot\vec{a} = \mu + i\xi$ (μ,ξ real >0), μ must equal 0 or 2π and $\vec{k}\cdot\vec{c}$ must be equal to 0 or π. Then, equation (83) reduces to

$$\alpha - \alpha' + e^{\xi}\left[e_5 + e_6 + e_{12} + 2(e_7 + e_8 + e_{13}) \cos \vec{k}\cdot\vec{b}\right] \pm 2e^{\xi/2}\left\{\left[e_9 + (e_{10} + e_{11})\cos \vec{k}\cdot\vec{c}\right] \cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2\right\} = 0, \qquad (85)$$

which is a quadratic equation in $e^{\xi/2}$ and the discussion is basically the same as for the case of the <u>ac</u> plane. For this case there is one surface state in the $\vec{k} \| \vec{a}^{-1}$ direction, two in the $\vec{k}\,||\,\vec{c}^{\,-1}$ direction and a surface band in $\vec{k}\,||\,\vec{b}^{\,-1}$ direction for each crystal orientation.

$$E\pm(\vec{k}\,||\,\vec{a}^{\,-1}) = \alpha + 2A_1\cosh(\xi_1) \pm 4B_1\cosh(\xi_1/2) + D_1 \qquad (86a)$$

$$E\pm(\vec{k}\,||\,\vec{b}^{\,-1}) = \alpha + 2A_2\cosh(\xi_2) \pm 4B_2\cosh(\xi_2/2) + D_2 \qquad (86b)$$

$$E\pm(\vec{k}\,||\,\vec{c}^{\,-1}) = \alpha + 2A_3\cosh(\xi_3) \pm 4B_3\cosh(\xi_3/2) + D_3 \qquad (86c)$$

where

$$\begin{aligned}
&A_1(\vec{k}\,||\,\vec{a}^{\,-1}) = e_5 + e_6 + e_{12} + 2(e_7 + e_8 + e_{13})\\
&A_2(\vec{k}\,||\,\vec{b}^{\,-1}) = e_5 + e_6 + e_{12} + 2(e_7 + e_8 + e_{13})\cos \vec{k}\cdot\vec{b}\\
&A_3(\vec{k}\,||\,\vec{c}^{\,-1}) = e_5 + 2e_7 + (e_6 + 2e_8 + e_{12} + 2e_{13})\cos \vec{k}\cdot\vec{c};\\
&\vec{k}\cdot\vec{c} = 0, \pi\\
&B_1(\vec{k}\,||\,\vec{a}^{\,-1}) = e_9 + e_{10} + e_{11} + e_{14}\\
&B_2(\vec{k}\,||\,\vec{b}^{\,-1}) = (e_9 + e_{10} + e_{11})\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2\\
&B_3(\vec{k}\,||\,\vec{c}^{\,-1}) = e_9 + e_{14} + (e_{10} + e_{11})\cos \vec{k}\cdot\vec{c};\quad k\cdot c = 0, \pi\\
&C = \alpha - \alpha' \quad \text{(cf. equation (84))}\\
&D_1(\vec{k}\,||\,\vec{a}^{\,-1}) = 2(e_2 + e_3 + 2e_4)\\
&D_2(\vec{k}\,||\,\vec{b}^{\,-1}) = 2\left[e_2 + (e_3 + 2e_4)\cos \vec{k}\cdot\vec{b}\right]\\
&D_3(\vec{k}\,||\,\vec{c}^{\,-1}) = 2\left[e_3 + (e_2 + 2e_4)\cos \vec{k}\cdot\vec{c}\right];\ \vec{k}\cdot\vec{c} = 0, \pi.
\end{aligned} \qquad (87)$$

The possible roots of equation (83), $e^{\xi/2}$, where $\xi = -i\vec{k}\cdot\vec{b}$ are

$$P_+ \equiv e^{\xi_i/2} = (-B_i \pm\sqrt{B_i^2 - A_iC}\,)/A_i;\ \xi_i = 2\ln P_+,\ i = 1,2,3 \qquad (88a)$$

$$P_- \equiv e^{\xi_i/2} = (+B_i \pm\sqrt{B_i^2 - A_iC}\,)/A_i;\ \xi_i = 2\ln P_-,\ i = 1,2,3. \qquad (88b)$$

As discussed above, the roots corresponding to $\vec{k}\cdot\vec{b} = 2\pi + i\xi$ for the (+) band are simply equal to the roots corresponding to the $\vec{k}\cdot\vec{b} = i\xi$ for the (-) band.

B. Numerical Calculations

The values of $e_l (l = 2 \text{ to } 14)$ for anthracene and naphthalene are taken from KRCJ and their method of calculation has been described therein. The values of e_n,

$$e_n = \langle \emptyset(\vec{r}) \mid V_n(\vec{r} - \vec{r}_n) \mid \emptyset(\vec{r}\ ) \rangle \tag{89}$$

were calculated for an extra electron and hole in both anthracene and naphthalene using a linear combination of neutral carbon $2p_z$ wave functions u_i to describe the molecular orbitals $\emptyset$.

$$\emptyset = \sum_i C_i u_i \tag{90}$$

where the C_i are Hückel coefficients neglecting overlap(29) and the u_i are a linear combination of four Slater wave functions.

$$u_i(\vec{r}) = (\hat{n}_i\cdot\vec{r}) \sum_{j=1}^{4} a_j (\alpha_j{}^5/\pi)^{1/2} \exp(-\alpha_j r) \tag{91}$$

where $\hat{n}_i$ is the unit vector defining the direction of the 2p orbital and the coefficients a_j and orbital exponents α_j are given by Clementi and Roothaan.(46) This form for $u_i(\vec{r})$ was used because it gives the best fit to the tail of the wave function at the large distances which occur in the evaluation of the resonance and overlap integrals of molecules in crystals (cf. KRCJ and Table II, p. 30).

The potential energy of a neutral molecule V_n is expressed as a linear combination of neutral-carbon-atom potentials (cf. KRCJ).

$$V_n = \sum_i V_i \tag{92}$$

where V_i is the Goeppert-Mayer and Sklar$^{(53)}$ potential of carbon atom i. Using equation (89) for u_i, this gives:

$$V_i = -e^2/r_i \Big(\sum_{k,l}\sum a_l \alpha_l^{5/2} a_k \alpha_k^{5/2}/\beta_{kl}^{5}\Big)^{-1} \sum_{k,l}\sum \exp(-2(\beta_{kl} r_i) \\ (a_k \alpha_k^{5/2} a_l \alpha_l^{5/2}/\beta_{kl}^{5}) \Big[4/3(\beta_{kl} r_i)^3 + 4\,(\beta_{kl} r_i)^2 + \\ 6\,\beta_{kl} r_i + 4\Big], \tag{93}$$

where $\beta_{kl} = \frac{1}{2}(\alpha_k + \alpha_l)$. Then substituting equation (90) and (92) into equation (89) one obtains:

$$e_n = \sum_{i,j,m}\sum\sum c_{\alpha i} c_{\alpha j} \langle u_i(\vec{r}-\vec{r}_i) \mid V_m(\vec{r}-\vec{r}_n-\vec{r}_m) \mid u_j(\vec{r}-\vec{r}_j)\rangle \tag{94}$$

where α indicates the number of the molecular orbital. For the two center integrals (those with both wave functions on the same atom, i = j, and the potential on a different molecule), the integral portion of equation (94) can be expanded as

$$-\pi^{-1}\Big[(\hat{n}_i \cdot \vec{R}_{im})^2/R_{im}^2\Big] A_{im} + (2\pi)^{-1}\Big[1-(\hat{n}_i \cdot \vec{R}_{im})^2/R_{im}^2\Big] \times \\ B_{im}, \tag{95}$$

where $\hat{n}_i$ is the unit vector defining the direction of orbital i, and $\vec{R}_{im}$ is the vector from atom i to atom m.

$$A_{im} = \int r_i^2 \cos^2 \gamma_i V_m \sum_k \sum_l a_k \alpha_k^{5/2} a_l \alpha_l^{5/2} \exp\left[-(\alpha_k + \alpha_l) r_i\right] d\tau$$

$$B_{im} = \int r_i^2 \sin^2 \gamma_i V_m \sum_k \sum_l a_k \alpha_k^{5/2} a_l \alpha_l^{5/2} \exp\left[-(\alpha_k + \alpha_l) r_i\right] d\tau \qquad (96)$$

where γ_i is the angle $\vec{r}_i$ makes with $\vec{R}_{im}$. A_{im} and B_{im} can be integrated analytically by carrying out the integration in elliptical coordinates, but since the result is a sum of many terms and there are 13 x 14 x 14 such integrals to be evaluated for anthracene, the results were computed using a CDC6600 which took about one minute. (The details of the integration are given in Appendix I, and the computer program in Appendix II.) The three center integrals were carried out numerically by a three dimensional Gaussian integration using 14^3 points. The programs are given in Appendix II and took about one hour on the CDC6600 for anthracene. The subroutine for the Gaussian integration was written by A. H. Stroud(54) and the coefficients were given by Stroud and Secrest.(55)

The three center integrals were carried out for wave functions on NN, NNN, and NNNN atoms with the potential on a second molecule and were calculated only when the distance between the midpoint of the two atoms and the potential function was less than 6.5 Å for the NN case and less than 5.2 Å for the NNN and NNNN cases. Neglecting integrals for which the distances are greater than these values results in an error of less than 0.1% in the energy.

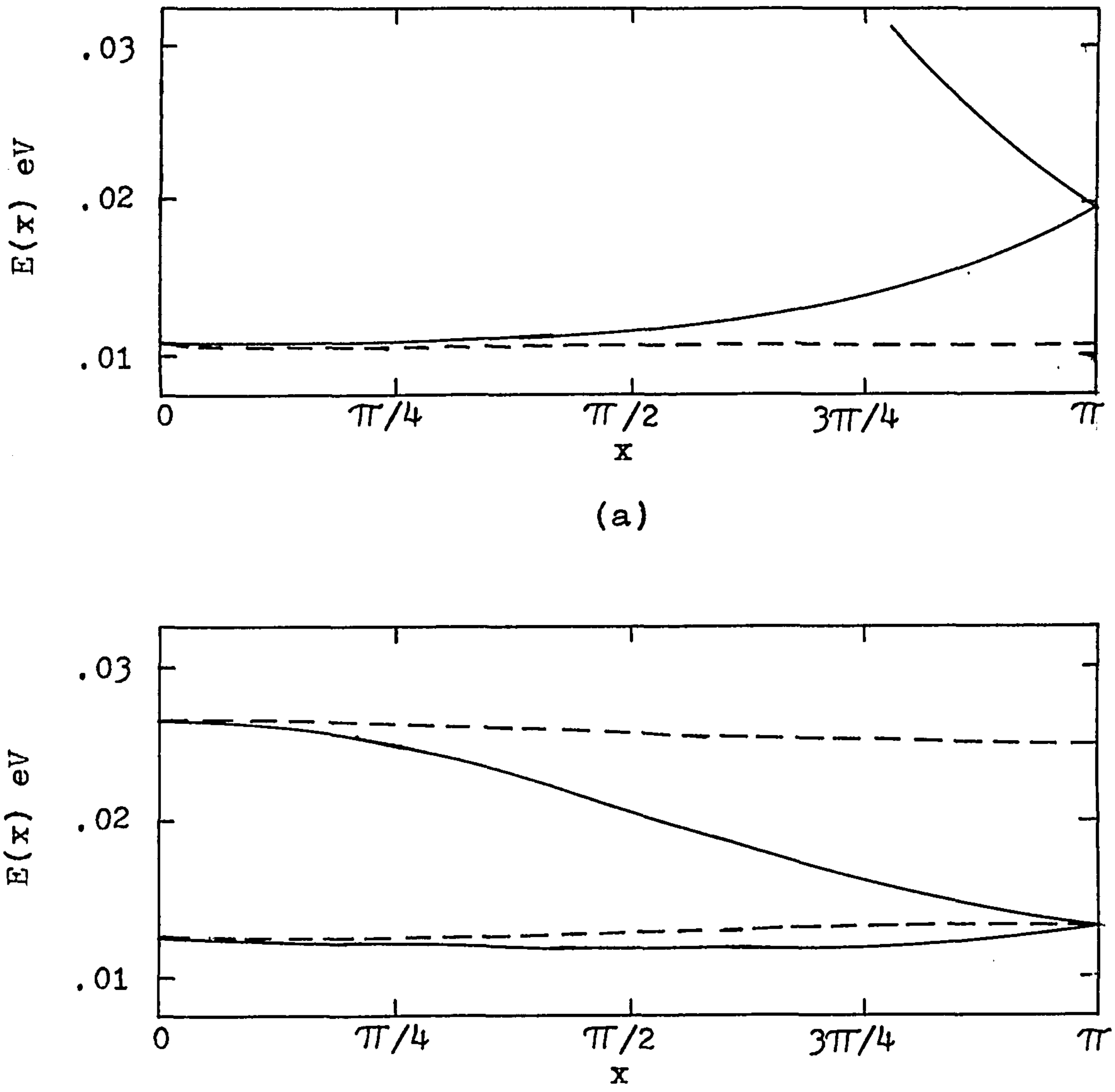
C. Numerical Results

The crystal constants and atomic coordinates used in these calculations for anthracene and naphthalene are given in Table I(50 - 52) (p. 29). Table IV gives the values of the resonance integrals, e_1, calculated in KRCJ as well as the integrals e_n calculated herein. The integrals are calculated between molecule one at the corner of the unit cell, and the neighboring molecules, two through fourteen as depicted in Fig. 2 (p. 23). The table gives the results of the calculation for the two-center integrals and for the two and three-center integrals combined.

The resultant surface bands (equations (71) and (86)) for an excess electron and hole are plotted in Figures 3, 4, and 5 in the reciprocal crystal axis directions. Figure 3 gives the electron bands in the <u>ac</u> plane of both anthracene and naphthalene. The naphthalene electron band extends in the $\vec{K} \| \vec{a}^{-1}$ and $\vec{K} \| \vec{c}^{-1}$ directions. In the $\vec{c}^{-1}$ direction the bands are very narrow (.001 eV for the E_+ band and .0015 eV for the E_- band) and are split by about .016 eV. In the $\vec{a}^{-1}$ direction, the bands have a width of .013 eV. Although surface bands do exist for the electron band of anthracene in the <u>ac</u> plane, they overlap with the bulk bands

Table IV. Intermolecular Resonance Integrals in Units of 10^{-4} eV

	Anthracene			Naphthalene		
Molecule number	e_1 (from KRCJ)	e_n (two-center intgrls	e_n (two & three center intgrls	e_1 (from KRCJ)	e_n (two-center intgrls	e_n (two & three center intgrls
			Hole			
2	-0.47	-0.37	-0.18	-0.36	-1.24	-0.94
3	-132.44	-41.26	-38.24	-120.97	-40.75	-39.53
4	-0.17	0.00	0.00	-1.76	0.00	0.00
5	0.20	-0.02	-0.02	0.27	-0.02	-0.02
6	-4.39	-0.18	-0.19	11.18	-0.30	-0.32
7	0.03	0.00	0.00	0.32	0.00	0.00
8	-0.03	0.00	0.00	0.05	0.00	0.00
9	-93.05	-78.88	-75.06	39.30	-70.20	-72.28
10	36.61	-1.38	-1.97	-42.50	0.15	-0.54
11	0.01	0.00	0.00	-0.02	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00
14	0.01	0.00	0.00	0.04	0.00	0.00
			Electron			
2	0.15	-0.37	-0.43	-5.60	-1.24	-1.28
3	71.61	-41.26	-34.49	22.77	-40.75	-33.89
4	-0.03	0.00	0.00	0.16	0.00	0.00
5	0.25	-0.02	-0.02	0.00	-0.02	-0.02
6	-0.74	-0.18	-0.17	3.51	-0.30	-0.28
7	0.04	0.00	0.00	-0.05	0.00	0.00
8	0.02	0.00	0.00	-0.03	0.00	0.00
9	-124.79	-78.88	-64.29	-52.46	-70.20	-57.20
10	2.48	-1.38	-0.48	-3.37	0.15	1.09
11	0.02	0.00	0.00	-0.03	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.01	0.00	0.00



(a)

(b)

Figure 3. The electron bands in the ac plane of anthracene (a), and of naphthalene (b) in the $\vec{k} \| \vec{a}^{-1}$ and $\vec{k} \| \vec{c}^{-1}$ directions. (Solid line: $x = \vec{k} \cdot \vec{a}$; dashed line: $x = \vec{k} \cdot \vec{c}$.)

as shown by the fact that the only possible solutions to equation (73) from 0 to $13\pi/18$ are real. This is represented by a discontinuity in the band plot. Since no solution of the form $\vec{k}\cdot\vec{b} = 2n\pi + i\xi$ exists for the naphthalene or anthracene hole bands on the surface of the ac plane, all solutions to equation (67) for $\vec{k}\cdot\vec{b}$ are real, and the surface bands lie completely within the bulk bands. This result allows for the trapping of electrons on the surface of naphthalene (but not anthracene), which would facilitate hole injection.

Figure 4 shows a plot of the anthracene and naphthalene hole surface bands and Figure 5 the electron surface bands in the bc plane. Naphthalene has a hole band in the $\vec{b}^{-1}$ direction with a width of .05 eV. There is also a surface state in the $\vec{c}^{-1}$ direction at $\xi = -i\vec{k}\cdot\vec{c} = \pi$, which lies .047 eV below the maximum of the band in the $\vec{b}^{-1}$ direction and which might serve as a hole trap facilitating electron injection from that surface. The electron bands are narrow and overlap into the bulk energy bands in the $\vec{b}^{-1}$ direction in the region where only real solutions to equation (88) exist. In the $\vec{c}^{-1}$ direction, two isolated surface states appear.

For anthracene in the bc plane, relatively wide surface bands exist (.034 eV for the hole band and .028 eV for the electron bands in the $\vec{b}^{-1}$ direction), but these overlap with the bulk bands at the discontinuity in the plot

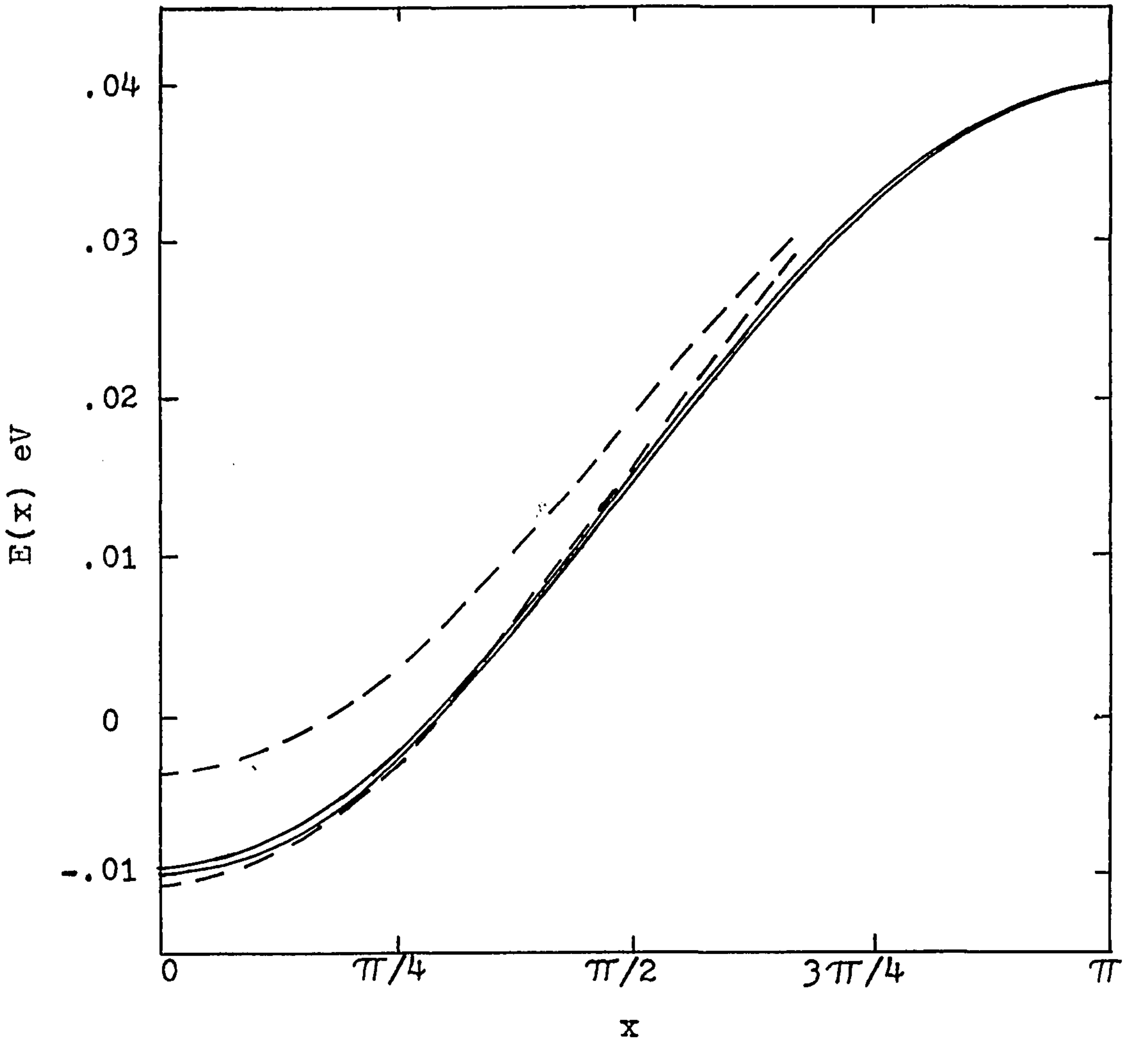


Figure 4. The hole bands in the bc plane of anthracene in the $\vec{k} \parallel \vec{b}^{-1}$ direction (dashed line: $x = \vec{k}\cdot\vec{b}$), and of naphthalene in the $\vec{k} \parallel \vec{b}^{-1}$ direction (solid line: $x = \vec{k}\cdot\vec{b}$).

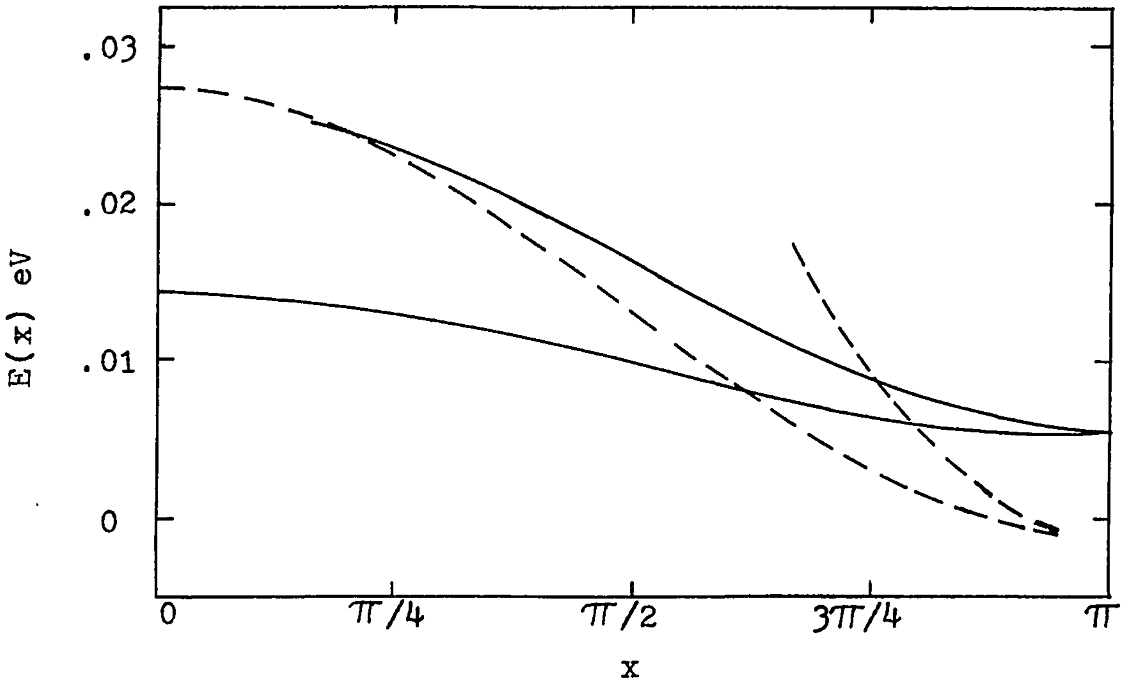


Figure 5. The electron bands in the *bc* plane of anthracene in the $\vec{k} \parallel \vec{b}^{-1}$ direction (dashed line: $x = \vec{k} \cdot \vec{b}$), and of naphthalene in the $\vec{k} \parallel \vec{b}^{-1}$ direction (solid line: $x = \vec{k} \cdot \vec{b}$).

for the reasons stated above. However, in both cases, isolated surface states exist in the $\vec{c}^{-1}$ direction. Table V summarizes the isolated surface states which appear in the bc plane in anthracene and naphthalene giving also their separation from the band in the $\vec{b}^{-1}$ direction.

In the ab plane, there are no solutions to equation (80) of the form $\vec{k}\cdot\vec{c} = n\pi + i\xi$, $\xi > 0$, except at isolated regions, for either the hole bands or the electron bands of anthracene and naphthalene. The possible values of $\vec{k}\cdot\vec{c}$, therefore, are all real at almost all points so that the bands are all overlapped with the bulk bands and surface states do not appear to be a likely source of carrier injection.

D. Mobility Calculations and Results

The carrier mobility was calculated for the two cases for which separated surface bands appeared. These include the electron surface band on the ac surface and the hole surface band on the bc surface for naphthalene. The mobility tensor was calculated in the constant free time approximation as in KRCJ, which assumes a constant isotropic relaxation time where $\tau(\vec{k}) = \tau_o$, and the components of the mobility tensor are:

$$\mu_{ij} = e\,\tau_o \langle V_i V_j \rangle /kT, \tag{97}$$

where V_i is the i^{th} component of the group velocity vector,

Table V. Isolated Surface States in the bc Place in Units of 10^{-4} eV.

Anthracene			Naphthalene		
Position	Energy	Separation from band edge	Position	Energy	Separation from band edge
	Hole			Hole	
$\vec{k}\cdot\vec{c} = \pi$	-113.67	77.60	$\vec{k}\cdot\vec{c} = \pi$	-73.19	472.19
	Electron			Electron	
$\vec{k}\cdot\vec{c} = \pi$	271.76	279.95	$\vec{k}\cdot\vec{c} = \pi$	247.97	535.52
			$\vec{k}\cdot\vec{c} = \pi$	172.33	611.16

$\vec{v}(\vec{k})$ associated with $\Psi(\vec{k})$:

$$\vec{v}(\vec{k}) = (1/\hbar)\ \vec{\nabla}_k E(\vec{k}). \tag{98}$$

The brackets represent the averaging over the Boltzmann distribution of electrons in the bands:

$$\langle v_i v_j \rangle = \frac{\int \left\{ \frac{\delta E_+}{\delta k_i} \frac{\delta E_+}{\delta k_j} \exp\left[-\beta E_+(\vec{k})\right] + \frac{\delta E_-}{\delta k_i} \frac{\delta E_-}{\delta k_j} \exp\left[-\beta E_-(\vec{k})\right] \right\} d\vec{k}}{\hbar^2 \int \left\{ \exp\left[-\beta E_+(\vec{k})\right] + \exp\left[-\beta E_-(\vec{k})\right] \right\} d\vec{k}}, \tag{99}$$

where $\beta = 1/kT$. The integration was carried out numerically on an IBM 360/50 computer. The trapezoidal rule was employed using 12 integration points per dimension. The coordinates chosen were the unit cell vectors $\vec{a}$ and $\vec{b}$ and the vector $\vec{c}'$, perpendicular to the ab plane. The integrations were carried out over the appropriate Brillouin zone for the surface in question and required only a few seconds of computer time.

The results are tabulated in Table VI along with the results of KRCJ for the appropriate bulk carrier mobilities. The hole mobility of naphthalene on the bc surface is the same as that calculated for the bulk, but the electron mobility of naphthalene on the ac surface is much greater.

Table VI. Components of the mobility tensor for naphthalene surface bands in the constant free time approximation in units of 10^{10} cm^2/sec^2.

Electron band in the ac plane			Hole band in the bc plane
$\langle v_a\ v_a \rangle$	$\langle v_a\ v_{c'} \rangle$	$\langle v_{c'}\ v_{c'} \rangle$	$\langle v_b\ v_b \rangle$
269	21.5	4.4	215

Electron band in the bulk (KRCJ)			Hole band in the bulk(KRCJ)
$\langle v_a\ v_a \rangle$	$\langle v_a\ v_{c'} \rangle$	$\langle v_{c'}\ v_{c'} \rangle$	$\langle v_b\ v_b \rangle$
39	-0.5	1	217

E. Concluding Remarks

The results are, of course, dependent upon the accuracy of the calculations of the resonance integrals, e_1, carried out in KRCJ and the integrals e_n calculated herein, as well as the magnitude of the effect of the approximations in theory mentioned above. Taking the possibility of these errors into account, it seems unlikely that they could change the nature of the results for the ab and ac planes. In the bc plane, however, the values of A (cf. equation (87) are so small that a slight change in their values (amounting to a few percent of the total energy), could make the difference between whether the surface band overlapped with the bulk band or was actually separated from it.

IV. THE EFFECT OF AN ELECTRIC FIELD ON THE SURFACE STATES OF ANTHRACENE AND NAPHTHALENE

The calculation of surface states in anthracene and naphthalene has led to the prediction of separated electron surface bands in the ac surface of naphthalene and separated hole surface bands in the bc surface of naphthalene. In all the other cases calculated, surface bands are either partially overlapped with the bulk bands or they do not occur at all (ie. there are no imaginary solutions of the form $\theta = \pi + i\xi$ for equations (67), (76) or (83)). However, if a perturbation were applied to the surface in the form of a trapped, charged ion, it should be possible to cause a surface band to separate from the bulk.

This chapter will be an attempt to calculate how large a perturbation would be necessary to cause a surface band to separate for those cases in which in the unperturbed state either only a partially overlapped surface band or no surface band appeared.

A. Method of calculation

1. ac surface

The assumption is made that the perturbation only affects the energy at the surface. Then the energy in the crystal is given as before by equation (65) while the energy for the surface is given by equation (66) with a perturbation added:

$$E_{\pm}(k) = \text{Equation (66)} + \lambda\,\text{Equation (66)}, \qquad (100)$$

where λ is the degree of perturbation which is to be determined. Subtracting equation (100) from equation (65) gives

$$\text{Equation (67)} - \lambda\,\text{Equation (66)} = 0, \qquad (101)$$

where $\alpha - \alpha'$ is given by equation (68) and

$$\alpha' = e_{n3} + 2(e_{n2} + e_{n4} + e_{n5} + e_{n6} + e_{n7} + e_{n8} + e_{n9} + e_{n10} + e_{n11} + e_{n12} + e_{n13} + e_{n14}). \qquad (102)$$

If $\vec{k}\cdot\vec{b}$ is of the form $i\xi$ with ξ real and positive (cf. above p. 38), and molecule 14 is neglected as before, then equation (101) reduces to

$$\begin{aligned}
&\alpha - \alpha' + (e^{\xi} - \lambda e^{-\xi})\Big[e_3 + 2e_4\cos\vec{k}\cdot\vec{c} + \\
&2e_7\cos\vec{k}\cdot\vec{a} + 2e_8\cos\vec{k}\cdot(\vec{a}+\vec{c}) + 2e_{13}\cos\vec{k}\cdot(\vec{a}-\vec{c})\Big] \\
&\pm 2(e^{\xi/2} - \lambda e^{-\xi/2})\Big[e_9\cos\vec{k}\cdot\vec{a}/2 + e_{10}\cos\vec{k}\cdot(\vec{a}/2 + \vec{c}) \\
&+ e_{11}\cos\vec{k}\cdot(\vec{a}/2 - \vec{c})\Big] - \lambda\Big\{\alpha' + 2\Big[e_2\cos\vec{k}\cdot\vec{c} + \\
&e_5\cos\vec{k}\cdot\vec{a} + e_6\cos\vec{k}\cdot(\vec{a} + \vec{c}) + e_{12}\cos\vec{k}\cdot(\vec{a} - \vec{c})\Big]\Big\} \\
&= 0. \qquad (103)
\end{aligned}$$

Solving for $e^{\xi/2}$ gives

$$e^{\xi/2} = \frac{\mp B_1 \pm \sqrt{B_1^2 - A_1\left[\hat{\mathcal{C}} - \lambda(\alpha' + D_1 + A_1 e^{-\xi} \pm 2B_1 e^{-\xi/2})\right]}}{A_1} \qquad (104)$$

where the definitions in equation (72) have been used.

In order for a surface band to separate from the bulk, ξ must be > 0 so that the right side of equation (104) must be > 1 in absolute value. If the right side of the equation is negative, $\vec{k}\cdot\vec{b}/2$ is chosen equal to $\pi + i\xi/2$ so that $\exp(\xi/2)$ is >1. This results in the following values for λ:

$$\lambda > \left| \frac{A_1 \pm 2B_1 + C}{\alpha' + D_1 + A_1 + 2B_1} \right| . \tag{105}$$

2. *ab* surface

The treatment of the *ab* surface is essentially the same as above. Instead of equation (100), the energy for the *ab* surface is given by

$$E_{\pm}(k) = \text{Equation } (75) + \lambda \,\text{Equation } (75). \tag{106}$$

This is subtracted from equation (65) to give

$$\text{Equation } (76) - \lambda \,\text{Equation } (75) = 0, \tag{107}$$

where $\alpha - \alpha'$ is given by equation (77) and

$$\alpha' = e_{n2} + e_{n6} + e_{n12} + 2(e_{n3} + e_{n4} + e_{n5} + 2e_{n7} + e_{n8} + 2e_{n9} + e_{n10} + e_{n11} + e_{n13}). \tag{108}$$

If $\vec{k}\cdot\vec{c}$ is of the form $i\xi$ with ξ real and positive and $\vec{k}\cdot\vec{a} = 2n\pi$, $n = 0,1,2,\ldots$ (cf. above p. 42), equation (107) reduces to

$$\alpha - \alpha' + (e^{\xi} - \lambda e^{-\xi})\left[e_2 + 2e_4\cos \vec{k}\cdot\vec{b} + e_6\right.$$

$$+ e_{12} + 2(e_8 + e_{13})\cos \vec{k}\cdot\vec{b} \pm 2(e_{10} + e_{11}) \times \cos \vec{k}\cdot\vec{b}/2\Big] - \lambda\Big\{\alpha' + 2\Big[e_5 + (e_3 + 2e_7) \times \cos \vec{k}\cdot\vec{b} \pm 2(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2)\Big]\Big\} = 0. \quad (109)$$

Solving for e^{ξ} gives

$$e^{\xi} = -\frac{C}{A_1 \pm B_1} + \lambda\left[\frac{e^{-\xi}(A_1 \pm B_1) + \alpha' + D_1 \pm 4(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2)}{A_1 \pm B_1}\right], \quad (110)$$

where the definitions in equation (79) have been used. As before, in order for a surface band to separate from the bulk, ξ must be > 0 so that the right side of equation (110) must be > 1 in absolute value. If the right side of equation (110) is negative, $\vec{k}\cdot\vec{c}$ is chosen equal to $\pi + i\xi$ so that $\exp(\xi) > 1$. This results in the following values for λ:

$$\lambda > \left|\frac{(A_1 \pm B_1) + C}{\alpha' + D_1 \pm 4(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2) + (A_1 \pm B_1)}\right|, \quad (111).$$

or

$$\lambda > \left|\frac{-(A_1 \pm B_1) + C}{\alpha' + D_1 \pm 4(e_9\cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2) - (A_1 \pm B_1)}\right|. \quad (112)$$

Equation (111) results when $\vec{k}\cdot\vec{c} = i\xi$, while equation (112) is used when $\vec{k}\cdot\vec{c} = \pi + i\xi$. It should be possible to satisfy both equation (111) and (112) with λ's of different signs, one of which will cause a surface band to separate in one direction while the other causes a surface band to separate in the other direction.

3. bc surface

The bc surface is virtually the same as the ac surface. Instead of equation (100), the energy for the bc surface is given by

$$E_{\pm}(\vec{k}) = \text{Equation (81)} + \lambda\, \text{Equation (81)}. \qquad (113)$$

Subtracting this from equation (65) gives

$$\text{Equation (83)} - \lambda\, \text{Equation (81)} = 0 \qquad (114)$$

where $\alpha - \alpha'$ is given by equation (84) and

$$\alpha' = 2(e_{n2} + e_{n3} + 2e_{n4}) + e_{n5} + e_{n6} + e_{n12} + 2(e_{n7} + e_{n8} + e_{n9} + e_{n10} + e_{n11} + e_{n13} + e_{n14}). \qquad (115)$$

If $\vec{k}\cdot\vec{a}$ is of the form $i\xi$ with ξ real and positive and $\vec{k}\cdot\vec{c} = 0$ or π (cf. above p. 44), equation (114) reduces to

$$\alpha - \alpha' + (e^{\xi} - \lambda e^{-\xi})\Big[e_5 + e_6 + e_{12} + 2(e_7 + e_8 + e_{13})\cos \vec{k}\cdot\vec{b}\Big] \pm 2(e^{\xi/2} - \lambda e^{-\xi/2})\Big\{\Big[e_9 + (e_{10} + e_{11})\cos \vec{k}\cdot\vec{c}\, \cos \vec{k}\cdot\vec{b}/2 + e_{14}\cos \vec{k}\cdot 3\vec{b}/2\Big] - \lambda\Big\{\alpha' + 2\Big[e_2\cos \vec{k}\cdot\vec{c} + e_3\cos \vec{k}\cdot\vec{b} + 2e_4\cos \vec{k}\cdot\vec{b}\, \cos \vec{k}\cdot\vec{c}\Big]\Big\} = 0. \qquad (116)$$

Solving for $e^{\xi/2}$ gives

$$e^{\xi/2} = \frac{\mp B_1 \pm\sqrt{B_1^2 - A_1\Big[C - \lambda(\alpha' + D_1 + A_1 e^{-\xi} \pm 2B_1 e^{-\xi/2})\Big]}}{A_1}, \qquad (117)$$

where the definitions in equation (87) have been used. In order for a surface band to separate from the bulk, ξ

must be >0 so that the right side of equation (117) must be >1 in absolute value. If the right side of the equation is negative, $\vec{K}\cdot\vec{a}/2$ is chosen equal to $\pi + i\,\xi/2$ so that $\exp(\xi/2)$ is >1. This results in the following values for λ:

$$\lambda > \left| \frac{A_1 \pm 2B_1 + C}{\alpha' + D_1 + A_1 \pm 2B_1} \right| . \tag{118}$$

B. Numerical results

1. ac surface

λ was calculated for the three cases in which surface bands do not separate in the ac surface. For anthracene, separation of a hole surface band required $\lambda > 0.98$, while separation of an electron surface band required $\lambda > 1.01$. For naphthalene, separation of a hole surface band required $\lambda > 1.07$. This implies that the energy of the surface would have to be perturbed by about 100% in order for a surface band to separate. Such a large change is hardly a small perturbation and doesn't permit treating the perturbed surface band in the same formalism as the unperturbed band. It is, therefore, not possible to conclude that the effect of a field on the surface would cause separation of a surface band using this treatment. For the naphthalene electron band, as shown in the previous chapter, a surface band separates even without a field.

2. ab surface

As mentioned above, in the ab surface it is possible for λ to be either positive or negative for any given case. λ was calculated for the $\vec{k} \parallel \vec{b}^{-1}$ direction. For the anthracene hole band, a value of $\lambda > 0.47$ was required to cause separation of a surface band to energies lower than those of the bulk band; to cause separation of a surface band to energies above those of the bulk band, a value of $\lambda < -2.5$ would be required. This latter value is certainly beyond the validity of the approximations of this treatment, while the former value of 0.47 is of questionable validity.

For the anthracene electron band, an interesting situation occurs. A value of $\lambda > 0.061$ causes the surface band to shift to energies above those of the bulk band for most of the band, and to energies below those of the bulk band for a small part of the band. A value of $\lambda < -0.023$ has the opposite effect. The surface band is shifted to energies below those of the bulk band for part of the band and above those of the bulk band for the other part of the band. This is a consequence of the fact that the numerator of equation (110), which is a function of $\vec{k}$, changes sign. This insures that for some values of $\vec{k}$ the right side of equation (110) will be < 1 in absolute value so that no separation of a surface band can occur.

For the naphthalene hole band, a value of $\lambda >$

0.17 causes a surface band to separate to energies below those of the bulk band, while a value of $\lambda < -0.23$ causes separation of a surface band to energies above those of the bulk band. These bands are plotted in Figure 6.

For the naphthalene electron bands, a value of $\lambda > 0.094$ causes separation of a surface band with energies below those of the bulk band, while a value of $\lambda < -0.153$ causes a surface band to separate with energies above those of the bulk band. These bands are plotted in Figure 7.

3. <u>bc</u> surface

λ was calculated for the $\vec{k} \| \vec{b}^{-1}$ direction for the three cases for which surface bands do not separate. For the anthracene hole band, the surface band is overlapped with the bulk band from $\vec{k} \cdot \vec{b} = 130^\circ$ to $\vec{k} \cdot \vec{b} \doteq 230^\circ$. The value of λ necessary to cause the surface band to separate at $\vec{k} \cdot \vec{b} = 230^\circ$ is 1.82 or greater. For the anthracene electron band, the surface band overlaps the bulk band from $\vec{k} \cdot \vec{b} = 0^\circ$ to $\vec{k} \cdot \vec{b} = 110^\circ$. In this case, a value of $\lambda > 1.25$ would be necessary to cause a surface band to separate at $\vec{k} \cdot \vec{b} = 0^\circ$. This represents an energy change at the surface of 182% for the electron band and of 125% for the hole band so that it is not possible to use this sort of treatment to predict separation of a surface band as a result of a field perturbation in these two cases.

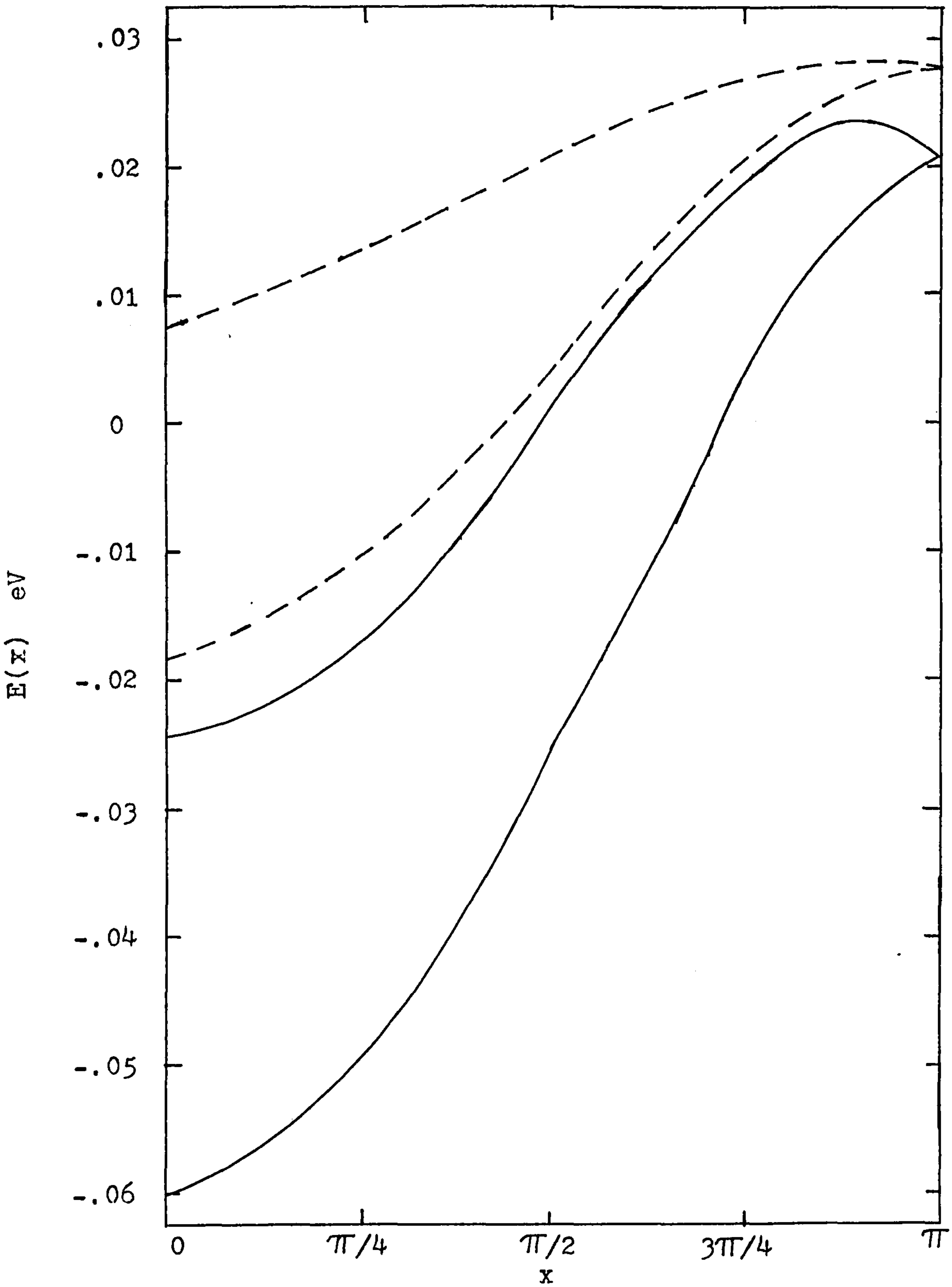


Figure 6. Naphthalene hole surface bands in the ab surface resulting from a perturbation λ. Solid line: λ = 0.17; dashed line: λ = -0.23; x = $\vec{k} \cdot \vec{b}$.

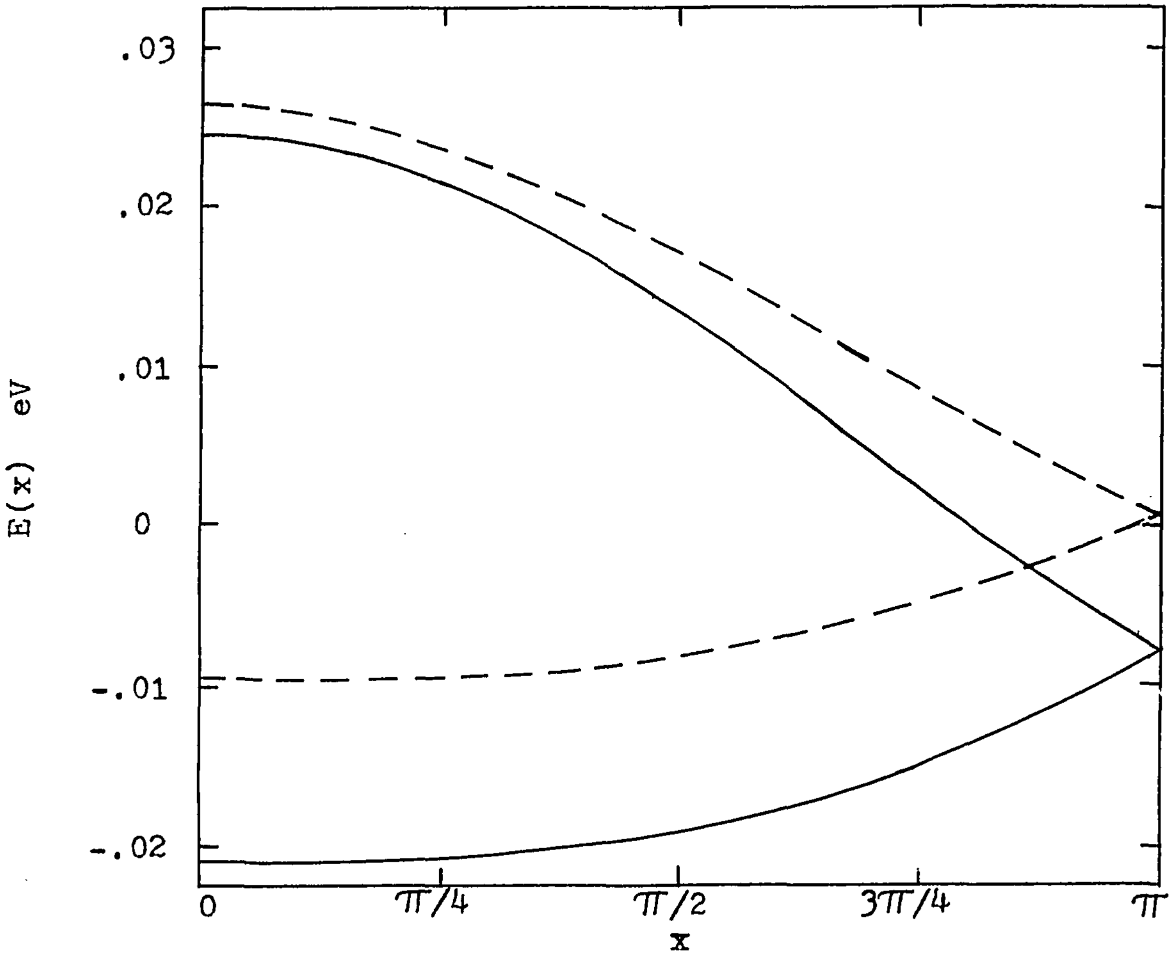


Figure 7. Naphthalene electron surface bands in the ab surface resulting from a perturbation λ. Solid line: $\lambda = 0.094$; dashed line: $\lambda = -0.15$; $x = \vec{k}\cdot\vec{b}$.

The naphthalene electron band has a nearly separated surface band which only overlaps the bulk band from $\vec{k} \cdot \vec{b} = 340^\circ$ to $\vec{k} \cdot \vec{b} = 360^\circ$. A value of $\lambda < -0.077$ causes the surface band to separate completely to energies above those of the bulk band. This band is plotted in Figure 8.

C. The relationship between λ and field

There are four cases where a small perturbation is clearly sufficient to cause separation of a surface band. These are the naphthalene hole band in the ab surface and the naphthalene electron band in both the ab and bc surfaces. The anthracene hole band in the ab surface is possibly separated. The energies to which these various values of λ correspond are summarized in Table VII. These, except for the naphthalene electron band on the bc surface for which the corresponding energy is 2.5×10^{-4} eV, are seen to be in the $(37 - 80) \times 10^{-4}$ eV range. The other cases, for which λ is about one or more, correspond to energies in the range 0.015 - 0.044 eV.

The strongest possible external applied electric field which will not cause dielectric breakdown, of the order of 10^5 volts/cm, will change the energy at the surface by only 10^{-6} - 10^{-7} eV. This can be seen from the calculations of Chapter II and may also be inferred by an order of magnitude calculation using the equation for the polarization energy, P:

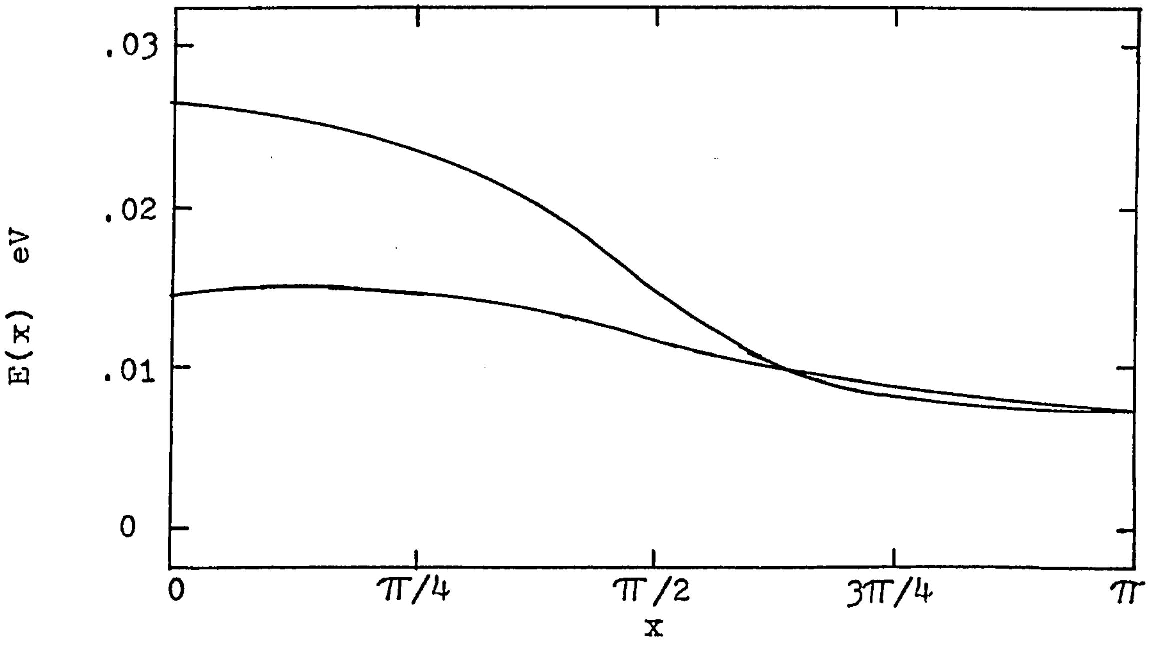


Figure 8. Naphthalene electron surface band in the bc surface resulting from a perturbation $\lambda = -0.077$; $x = \vec{k}\cdot\vec{b}$.

Table VII. The degree of perturbation, λ, and the corresponding energy change, E (in units of 10^{-4} eV), required to cause a surface band to separate for the three surfaces of anthracene and naphthalene.

	Surface								
	ac			ab			bc		
Band	$\vec{k}\cdot\vec{a}$	λ	E	$\vec{k}\cdot\vec{b}$	λ	E	$\vec{k}\cdot\vec{b}$	λ	E
Anthracene	0	0.98	-438	0	0.47	-46	230	1.82	-206
hole	360	0.95	-212	0	-2.50	37			
Anthracene	0	0.99	-337		b		0	1.25	-375
electron	360	1.01	152				180	0.38	
Naphthalene	0	1.07	-315	0	0.17	-80		a	
hole	360	1.07	-302	0	-0.23	75			
Naphthalene		a		0	0.094	-46	340	-0.077	2.5
electron				0	-0.153	68			

a. A surface band separates in the absence of any perturbation.
b. No perturbation effects separation of a surface band.

$$P = -\tfrac{1}{2}\alpha_{ij}F_iF_j + \text{higher order terms} \tag{119}$$

where α_{ij} is the polarizability tensor and F_i is the i^{th} component of the electrostatic fields. For naphthalene, the principal polarizabilities, α_1, α_2, α_3, lying along the principal axes of the molecule, are 21.5, 17.6, and 10.1 $\mathring{A}^3$, respectively.(56) For anthracene they are 33.9, 29.2, and 12.9 $\mathring{A}^3$, respectively.(57)

If a charged ion is adsorbed on the surface of the crystal, the polarization energy is given by summing over the polarization energy for each molecule. The closest molecule will have a polarization energy approximately given by

$$P = -e^2\alpha/2r^4 \tag{120}$$

where e is the charge of an electron, r is the distance between the center of charge and the centers of the molecule, and α is now an average polarizability. If the radius of the ion is 1 Å, equation (120) yields a value of 118 eV for naphthalene and 181 eV for anthracene! This corresponds to a field of the order of 10^9 volts/cm. Although such an energy change may well cause a surface band to separate, it is not possible to predict this using the present approach, nor would it be possible to calculate the energy of such a surface band relative to the bulk band.

There is also the possibility that the localization of a charge on the surface might itself cause the separation of a surface band. Such an ionized anthracene or naphthalene molecule would polarize the molecules around it changing the energy at the surface. The polarization energy of such an ionized molecule depends, of course, upon which surface of anthracene or naphthalene is considered, but it was calculated to be in the range of 0.7 eV for the ac surface of naphthalene to 1.2 eV for the ab surface of anthracene. This again, is somewhat higher than the energy changes required in the treatment above by two to three orders of magnitude.

V. CONCLUSION

The purpose of this work has been to investigate the possibility of the existence of surface states in organic crystals, in particular, anthracene and naphthalene. The bulk energy band structure of these crystals is already known and it is hoped that a knowledge of the energy band structure of their surfaces will lead to further insight into their electronic properties, especially in view of the fact that biological substances of similar structure may have analagous properties.

Although separated surface bands have been predicted only for the electron band in the <u>ac</u> surface and the hole band in the <u>bc</u> surface of naphthalene, the possibility of surface bands separating for other cases has been discussed. There are several cases in which surface bands only partially overlap the bulk bands (cf. Figures 3,4, and 5). It has been shown that a perturbation of the surface may be sufficient to cause these to separate completely. Even for some cases in which no surface bands were separated, it was shown that only a slight perturbation of the surface energy relative to the bulk would be sufficient to cause separation.

The effect of electric fields on these crystals has also been explored. It was shown that an applied d.c. field, as high as 10^5 volts/cm, produces a very slight effect on either the bulk bands or the surface bands of these crystals. This is a consequence of the very low interaction between neighboring molecules in the crystal. The field resulting from an adsorbed ion, however, presents a different picture. The field of such an ion is so large that its effect on the surface molecules is far too great to treat using a perturbation approach. Its field falls off as r^{-4}, however, so that by the second layer of molecules its effect is reduced by a factor of 10^3 to 10^4. By further developing the methods initiated here, it should not be too difficult to obtain a better understanding of the effect of such an adsorbed ion on the energy bands of the crystal.

It might also be pointed out that these calculations are certainly open to further refinements. The results of more refined calculations may lead to the prediction of complete separation of surface bands for certain cases in which these calculations did not. This is particularly true for those cases pointed out in Chapter III where a slight change in the calculated value of the energy would lead to a separated surface band.

For one, the effect of vibrations has been neglected here, and future work should include this. Also, the development and use of better molecular wave functions, which would allow calculation of the necessary integrals without resorting to the evaluation of the interaction between each pair or triplet of atoms within two molecules, is desireable. This would greatly reduce the amount of computer time necessary for some of these calculations.

A final suggestion for future work would be the calculation of the exciton surface bands, since excitons are believed to play a major role in the electronic properties of molecular crystals.

In any case, the method developed here provides a rather convenient, straight-forward formalism for calculating the surface bands of molecular crystals. In the event that the bulk bands are known, use of integrals already calculated simplifies the procedure so that the difficult problem of a three dimensional crystal made up of molecules with many atoms becomes tractable.

APPENDIX I

A. Evaluation of the overlap integrals, A_{ij} and B_{ij}

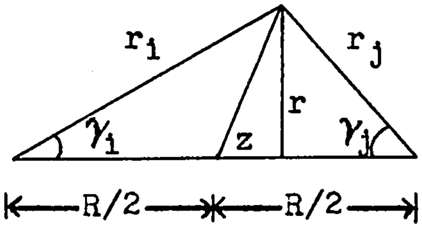
The integrals to be solved, exclusive of constants and summations, are of the form (cf. eqtns. (48) and (49))

$$\int r_i r_j \cos\gamma_i \cos\gamma_j \exp(-\alpha r_i - \beta r_j)\, d\tau \tag{121}$$

and

$$\int r_i r_j \sin\gamma_i \sin\gamma_j \exp(-\alpha r_i - \beta r_j)\, d\tau \tag{122}$$

where α and β are constants and r_i, r_j, γ_i, and γ_j are defined in the accompanying diagram.



Converting to confocal elliptical coordinates

$$\lambda = (r_i + r_j)/R, \quad \mu = (r_i - r_j)/R,$$
$$d\tau = R^3/8\,(\lambda^2 - \mu^2)\, d\lambda\, d\mu\, d\phi. \tag{123}$$

From the diagram it is seen that

$$r_i \cos\gamma_i = R/2 + z, \tag{124}$$

$$r_j \cos\gamma_j = R/2 - z, \tag{125}$$

and so

$$r_i r_j \cos\gamma_i \cos\gamma_j = R^2/4 - z^2. \tag{126}$$

Since

$$r_i^2 = r^2 + (z + R/2)^2 \tag{127}$$

and

$$r_j^2 = r^2 + (z - R/2)^2, \tag{128}$$

$$r_i^2 - r_j^2 = 2zR = \lambda\mu R^2 \text{ (from eqtn. (123))} \tag{129}$$

and

$$z = \lambda \mu R/2. \tag{130}$$

Substituting this into eqtn. (126) gives

$$r_i r_j \cos\gamma_i \cos\gamma_j = R^2/4(1 - \lambda^2\mu^2). \tag{131}$$

From eqtn. (123)

$$r_i = (\lambda + \mu)R/2, \quad r_j = (\lambda - \mu)R/2. \tag{132}$$

Thus, eqtn. (121) becomes

$$\int_0^2 \int_{-1}^{+1} \int_1^{\infty} d\lambda\, d\mu\, d\phi (R^5/32)(\lambda^2 - \mu^2)(1 - \lambda^2\mu^2) \text{ x }$$

$$\exp\left[-\lambda R/2(\alpha + \beta) - \mu R/2(\alpha - \beta)\right] . \tag{133}$$

From the diagram above, it is seen that

$$r_i \sin\gamma_i = r_j \sin\gamma_j = r. \tag{134}$$

From eqtns. (127) and (128)

$$r^2 = (r_i^2 + r_j^2)/2 - z^2 - R^2/4. \tag{135}$$

Substituting $(r_i^2 + r_j^2)$ from eqtn. (132), and z^2 from eqtn. (130) into eqtn. (135) gives

$$r_i r_j \sin\gamma_i \sin\gamma_j = r^2 = (R^2/4)(\lambda^2 - 1)(1 - \mu^2). \tag{136}$$

Thus, eqtn. (122) becomes

$$\int_0^2 \int_{-1}^{+1} \int_1^{\infty} d\lambda\, d\mu\, d\phi (R^5/32)(\lambda^2 - \mu^2)(\lambda^2 - 1)(1 - \mu^2) \text{ x }$$

$$\exp\left[-\lambda R/2(\alpha + \beta) - \mu R/2(\alpha - \beta)\right] . \tag{137}$$

B. <u>Evaluation of the coulomb integrals, A_{ij} and B_{ij}</u>

The integrals to be solved, exclusive of constants and summations, are of the form (cf. eqtn. (96)

$$\int r_i^2 \cos^2\gamma_i \exp(-2\alpha r_i - 2\beta r_j)(4/3\beta^3 r_j^2 + 4\beta^2 r_j + 6\beta + 4/r_j)\, d\tau \tag{138}$$

and

$$\int r_1^2 \sin^2\gamma_1 \exp(-2\alpha r_1 - 2\beta r_j)(4/3\beta^3 r_j^2 + 4\beta^2 r_j + 6\beta + 4/r_j)\, d\tau . \qquad (139)$$

Substitution of eqtn. (130) into eqtn. (124) gives

$$r_1 \cos\gamma_1 = R/2(1 + \lambda\mu). \qquad (140)$$

Substituting eqtns. (123), (132), and (140) into eqtn. (138) gives

$$\int_0^2 \int_{-1}^{+1} \int_1^{\infty} d\lambda\, d\mu\, d\phi (R^5/32)(\lambda^2 - \mu^2)(1 + \lambda\mu)^2 \times \exp\left[-\lambda R(\alpha + \beta) - \mu R(\alpha - \beta)\right] \left[(4/3)\beta^3(\lambda - \mu)^2 R^2/4 + 4\beta^2(\lambda - \mu)R/2 + 6\beta + 4/(\lambda - \mu)(R/2)\right] . \qquad (141)$$

Substitution of eqtns. (123), (132), and the right side of eqtn. (136) (cf. eqtn. (133)) into eqtn. (139) gives

$$\int_0^2 \int_{-1}^{+1} \int_1^{\infty} d\lambda\, d\mu\, d\phi (R^5/32)(\lambda^2 - \mu^2)(\lambda^2 - 1)(1 - \mu^2) \times \exp\left[-\lambda R(\alpha + \beta) - \mu R(\alpha - \beta)\right]\left[(4/3)\beta^3(\lambda - \mu)^2 R^2/4 + 4\beta^2(\lambda - \mu)R/2 + 6\beta + 4/(\lambda - \mu)(R/2)\right] . \qquad (142)$$

Eqtns. (133), (137), (141), and (142) can be evaluated by use of the standard exponential integrals

$$\int_1^{\infty} x^n e^{-ax} dx = \frac{n!\, e^{-a}}{a^{n+1}} \sum_{k=0}^{n} \frac{a^k}{k!} \qquad (143)$$

$$\int_{-1}^{+1} x^n e^{-ax} dx = (-1)^{n+1} \frac{n!\, e^{a}}{-a^{n+1}} \sum_{k=0}^{n} \frac{-a^k}{k!} - \frac{n!\, e^{-a}}{a^{n+1}} \sum_{k=0}^{n} \frac{a^k}{k!} . \qquad (144)$$

APPENDIX II LIST OF FORTRAN IV PROGRAMS

```
THIS PROGRAM CALCULATES THE FIRST AND SECOND ORDER PERTURBATION ENERGY OF AN
ANTHRACENE CRYSTAL AS A FUNCTION OF AN APPLIED D-C ELECTRIC FIELD ORIENTED IN
ONE OF THREE DIRECTIONS.  THE CRYSTAL HAS AN ELECTRON BAND CONSTRUCTED FROM
THE HUCKEL MOLECULAR ORBITALS CONTAINING ONE EXTRA ELECTRON, AND A HOLE BAND
CONSTRUCTED FROM THE HUCKEL MOLECULAR ORBITALS CONTAINING ONE LESS ELECTRON.

      COMMON N1(3), N2(3), ALPHA(4), AA(4), ALPHA1(6), A1(6), C1(6),
     1-D1(6), N1N2
      DIMENSION I7(14), REP(14,4), C(14,14), M(14),RA(14,3),RB(14,14,3),
     1 S(14,14), A(14), B(14), DLNH(7), DLNE(14),R1(3), R2(3),
     2RA1(14,3), RB2(14,14,3), H1H(14,3), H1E(14,3), H(8,3), H2H(14,3),
     3H2E(14,3), HH(7,3),HE(14,3), ENRG1H(14,3), ENRG2H(14,3),
     4ENRG1E(14,3), ENRG2E(14,3), SUM1H(3), SUM2H(3), SUM1E(3),SUM2E(3),
     5SUM1HN(3), SUM2HN(3), SUM1EN(3), SUM2EN(3), SUM1(8),
     6HENRG1(14,3), HENRG2(14,3), EENRG1(14,3), EENRG2(14,3), HSUM1(3),
     7HSUM2(3),HSUM1N(3),HSUM2N(3),ESUM1(3),ESUM2(3),ESUM1N(3),ESUM2N(3)
      DOUBLE PRECISION ALPHA, ALPHA1, AA, A1, N1, N2, N1N2, RA, RB, S,
     1DLNH, DLNE, RA1, RB2, H1H, H1E, H, H2H, H2E, HH, HE, ENRG2H,
     2ENRG1H, ENRG1E, ENRG2E, FIELD1, FIELD2, SUM1H, SUM2H, SUM1E,
     3SUM2E, GAMMA, SUM1HN, SUM2HN, SUM1EN, SUM2EN, SUM1, PRODH, PRODE,
     4HENRG1, HENRG2, EENRG1, EENRG2, HSUM1, HSUM2, HSUM1N, HSUM2N,
     5ESUM1, ESUM2, ESUM1N, ESUM2N
      INTEGER A, B
      REAL M

READ THE VALUES OF THE CORRECT HUCKEL COEFFICIENTS,NEGLECTING ANY OVERLAP, AND
THEIR CORRESPONDING REPRESENTATION.

      READ(5,101) I7, ((REP(I,J),J=1,4),I=1,14), C, M
101   FORMAT (7I1, 31I2/ 32I2/ (7F9.6))
READ VALUES OF PARAMETERS FOR CALCULATING OVERLAP INTEGRALS
      READ(5,102) ALPHA, AA
102   FORMAT (4F7.4, 4F8.5)
READ COORDINATES OF THE CORNER ANTHRACENE MOLECULE IN ANGSTROMS
      READ(5,103) N1, ((RA1(J,I1), I1=1,3), J=1,14)
103   FORMAT (3F7.4)
READ INDICES FOR EXCITED STATE ORBITALS
      READ(5,203) (A(L), B(L), L=1,14)
203   FORMAT (I1, I2)
WRITE HEADINGS
      WRITE(6,104)
104   FORMAT (1H1, 3X, 1HI, 8X, 4HM(I), 9X, 6HC(I,1), 8X, 6HC(I,5), 8X,
     16HC(I,9),7X, 7HC(I,13),9X, 3HREP, 7X,22HS = 0.000 ATOMIC UNITS//)
WRITE VALUES OF ENERGY LEVELS AND COEFFICIENTS
      WRITE(6,105)(I7(I),M(I),(C(I,J),J=1,14,4),(REP(I,J),J=1,4),I=1,14)
105   FORMAT (1H , I4, 5F14.6, 5X, 4I2)
WRITE HEADINGS FOR COORDINATES
      WRITE(6,106)
106   FORMAT (1H0, 12X, 29HCOORDINATES OF MOLECULE 1 (A), 15X, 29HCOORDI
     1NATES OF MOLECULE 1(AU)/5H ATOM, 7X, 5HRA(X), 8X, 5HRA(Y), 8X,
     2 5HRA(Z), 13X, 5HRA(X), 8X, 5HRA(Y), 8X, 5HRA(Z)//)
      CALL COORD (RA, RB, N1, N2, N1N2, RA1, RB2)
      DO 71 J = 1,14
 71   WRITE(6,17) J, (RA1(J,I1), I1=1,3), (RA(J,I1), I1=1,3)
 17   FORMAT (1H , I3, 1X, 3F13.5, 5X, 3F13.5)
      WRITE(6,108) N1, N2, N1N2
108   FORMAT (1H0, 8X, 29HNORMAL TO PLANE OF MOLECULE A, 15X, 29HNORMAL
     1TO PLANE OF MOLECULE B/ 1H , 7X, 5HN1(X), 8X, 5HN1(Y), 8X, 5HN1(Z)
```

```
     2, 13X, 5HN2(X), 8X, 5HN2(Y), 8X, 5HN2(Z), 8X, 5HN1*N2/ 1H0,
     3 3F13.5, 5X, 4F13.5)
      DO 72 I2 = 2,14
      WRITE(6,16) I2, I2
   16 FORMAT(1H0, 11X, 23HCOORDINATES OF MOLECULE, I3, 1X, 3H(A),  14X,
     1 23HCOORDINATES OF MOLECULE, I3, 4H(AU)/5H ATOM, 7X, 5HRB(X), 8X,
     2 5HRB(Y), 8X, 5HRB(Z), 13X, 5HRB(X), 8X, 5HRB(Y), 8X, 5HRB(Z)//)
      DO 701 J = 1,14
  701 WRITE(6,107) J, (RB2(I2,J,I1), I1=1,3), (RB (I2,J,I1), I1=1,3)
  107 FORMAT (1H , I3, 1X, 3F13.5, 5X, 3F13.5)
      IF (I2.NE.2.AND.I2.NE.5.AND.I2.NE.8.AND.I2.NE.11) GO TO 72
      WRITE(6,161)
  161 FORMAT (1H1)
   72 CONTINUE
      WRITE(6,109) ALPHA, AA
  109 FORMAT (1H1, 13X, 47HPARAMETERS FOR CALCULATION OF OVERLAP INTEGRA
     1LS/ 9H0 ALPHA =, 4(F8.4, 3X)/ 9H0      A =, 4(F9.5, 2X))
      CALL PRMTRS (ALPHA, AA, C1, D1, A1, ALPHA1)
      WRITE(6,110) C1, D1, A1, ALPHA1
  110 FORMAT (9H0     C1 =, 6(F8.4, 3X)/ 9H0     D1 =, 6(F8.4, 3X)/
     1 9H0     A1 =, 6F11.7/ 9H0ALPHA1 =, F8.4, 5F11.4)
BEGIN CALCULATIONS OF THE VARIOUS INTEGRALS

      DO 600 I2 = 2,14
      DO 200 J = 1,14
      DO 200 K = 1,14
      DO 20 I1 = 1,3
      R1(I1) = RA(J,I1)
   20 R2(I1) = RB(I2,K,I1)
      N = 1
      IF (I2.EQ.9.OR.I2.EQ.10.OR.I2.EQ.11.OR.I2.EQ.14) N = 2
      CALL OVRLP(S(J,K), R1, R2, N)
  200 CONTINUE
      WRITE(6,112) I2
  112 FORMAT(68H1OVERLAP INTEGRAL FOR AN ATOM ON MOLECULE 1 WITH AN ATOM
     1 ON MOLECULE, I3/)
      CALL OUTPT1 (S, 14, 14)
      DO 100 N = 7,8
      SUM1(N) = 0.0
      DO 100 L = 1,14
      DO 100 M1 = 1,14
  100 SUM1(N) = SUM1(N) + C(N,L)*C(N,M1)*S(L,M1)
      PRODH = SUM1(7)
      PRODE = SUM1(8)
      WRITE(6,666) PRODH, PRODE
  666 FORMAT(28H0OVERLAP OF HOLE FUNCTION = , 1PE11.4, 5X,
     1 31HOVERLAP OF ELECTRON FUNCTION = , E11.4)
      DO 600 I1 = 1,3
      DO 300 I = 7,8
      H(I,I1) = 0.0
      DO 300 J = 1,14
      DO 300 K = 1,14
  300 H(I,I1) = H(I,I1)+C(I,J)*C(I,K)*S(J,K)*(RA(J,I1)+RB(I2,K,I1))/2.0
      H1H(I2,I1) = H(7,I1)*DSQRT(2.0D0)
      H1E(I2,I1) = H(8,I1)*DSQRT(2.0D0)
      H2H(I2,I1) = 0.0
      H2E(I2,I1) = 0.0
      DO 59 L = 1,7
```

```
      IA = A(L)
      IB = B(L)
      HH(L,I1) = 0.0
      DO 501 J = 1,14
      DO 501 K = 1,14
  501 HH(L,I1)=HH(L,I1)+C(IA,J)*C(IB,K)*S(J,K)*(RA(J,I1)+RB(I2,K,I1))/2.
      IF (I1.GT.1.OR.I2.GT.2) GO TO 59
      CALL DLE(IA, IB, M, DLNH(L))
   59 H2H(I2,I1) = H2H(I2,I1) + 2.0*HH(L,I1)**2/DLNH(L)
      DO 60 L = 8,14
      IA = A(L)
      IB = B(L)
      HE(L,I1) = 0.0
      DO 500 J = 1,14
      DO 500 K = 1,14
  500 HE(L,I1)=HE(L,I1)+C(IB,J)*C(IA,K)*S(J,K)*(RA(J,I1)+RB(I2,K,I1))/2.
      IF (I1.GT.1.OR.I2.GT.2) GO TO 60
      CALL DLE(IA, IB, M, DLNE(L))
   60 H2E(I2,I1) = H2E(I2,I1) + 2.0*HE(L,I1)**2/DLNE(L)
  600 CONTINUE

      WRITE(6,21)
   21 FORMAT (1H1, 50X, 9HHOLE BAND)
      WRITE(6,210)
  210 FORMAT(1H0,13X,31HFIRST ORDER PERTURBATION ENERGY,22X,32HSECOND OR
     1DER PERTURBATION ENERGY//3H I2,7X,8HH1(I2,X),8X,8HH1(I2,Y),8X,
     2 8HH1(I2,Z),13X,8HH2(I2,X),8X,8HH2(I2,Y),8X,8HH2(I2,Z)/)
      DO 700 I2 = 2,14
  700 WRITE(6,111) I2, (H1H(I2,I1), I1=1,3), (H2H(I2,I1), I1=1,3)
  111 FORMAT (1H , I2, 1P3E16.4, 5X, 3E16.4)
WRITE HEADINGS
      WRITE(6,212)
  212 FORMAT(54H0PERTURBATION ENERGY OF CRYSTAL IN CM-1 IN A FIELD OF-//
     11H0,17X,23HONE MILLION VOLTS/METER,30X,23HTEN MILLION VOLTS/METER/
     2)
      FIELD1 = 8065.73*0.529167*1.0D-4
      FIELD2 = 8065.73*0.529167*1.0D-3
      GAMMA = -2.36*8065.73
      DO 90 I2 = 2,14
      DO 91 I1 = 1,3
      ENRG1H(I2,I1) = -FIELD1*H1H(I2,I1) + FIELD1**2*H2H(I2,I1)/GAMMA
   91 ENRG2H(I2,I1) = -FIELD2*H1H(I2,I1) + FIELD2**2*H2H(I2,I1)/GAMMA
   90 WRITE(6,113) I2, (ENRG1H(I2,I1), I1=1,3), (ENRG2H(I2,I1), I1=1,3)
  113 FORMAT (1H , I2, 1P3E16.4, 5X, 3E16.4)
      DO 76 I1 = 1,3
      SUM1H(I1) = 0.0
      SUM2H(I1) = 0.0
      DO 75 I2 = 2,14
      SUM2H(I1) = SUM1H(I1) + ENRG1H(I2,I1)
   75 SUM2H(I1) = SUM2H(I1) + ENRG2H(I2,I1)
      SUM1H(I1) = 4.0*SUM1H(I1) - 2.0*(ENRG1H(2,I1) + ENRG1H(3,I1) +
     1 ENRG1H(5,I1) + ENRG1H(6,I1) + ENRG1H(12,I1))
      SUM2H(I1) = 4.0*SUM2H(I1) - 2.0*(ENRG2H(2,I1) + ENRG2H(3,I1) +
     1 ENRG2H(5,I1) + ENRG2H(6,I1) + ENRG2H(12,I1))
      SUM1HN(I1) = SUM1H(I1) - 8.0*(ENRG1H(9,I1) + ENRG1H(10,I1) +
     1 ENRG1H(11,I1) + ENRG1H(14,I1))
   76 SUM2HN(I1) = SUM2H(I1) - 8.0*(ENRG2H(9,I1) + ENRG2H(10,I1) +
     1 ENRG2H(11,I1) + ENRG2H(14,I1))
```

```
      WRITE(6,114) SUM1H, SUM2H
  114 FORMAT(1H0,6HSUM+ =,2(1PE12.4,4X),E12.4,1X,4HCM-1,3E16.4,1X,4HCM-1
     1)
      WRITE(6,115) SUM1HN, SUM2HN
  115 FORMAT(1H0,6HSUM- =,2(1PE12.4,4X),E12.4,1X,4HCM-1,3E16.4,1X,4HCM-1
     1/)
      CM = 0.806573
      DO 10 I2 = 2,14
      DO 11 I1 = 1,3
      HENRG1(I2,I1) = ENRG1H(I2,I1)/CM
   11 HENRG2(I2,I1) = ENRG2H(I2,I1)/CM
   10 WRITE(6,113) I2, (HENRG1(I2,I1), I1=1,3), (HENRG2(I2,I1), I1=1,3)
      DO 12 I1 = 1,3
      HSUM1(I1) = SUM1H(I1)/CM
      HSUM2(I1) = SUM2H(I1)/CM
      HSUM1N(I1) = SUM1HN(I1)/CM
   12 HSUM2N(I1) = SUM2HN(I1)/CM
      WRITE(6,411) HSUM1, HSUM2
  411 FORMAT(1H0, 6HSUM+ =, 2(1PE12.4,4X), E12.4, 1X, 6H10-4EV, E14.4,
     1 2E16.4, 1X, 6H10-4EV)
      WRITE(6,511) HSUM1N, HSUM2N
  511 FORMAT(1H0, 6HSUM- =, 2(1PE12.4,4X), E12.4, 1X, 6H10-4EV, E14.4,
     1 2E16.4, 1X, 6H10-4EV)
      WRITE(6,22)
   22 FORMAT (1H1, 48X, 13HELECTRON BAND)
      WRITE(6,210)
      DO 800 I2 = 2,14
  800 WRITE(6,111) I2, (H1E(I2,I1), I1=1,3), (H2E(I2,I1), I1=1,3)
WRITE HEADINGS
      WRITE(6,212)
      DO 92 I2 = 2,14
      DO 93 I1 = 1,3
      ENRG1E(I2,I1) = -FIELD1*H1E(I2,I1) + FIELD1**2*H2E(I2,I1)/GAMMA
   93 ENRG2E(I2,I1) = -FIELD2*H1E(I2,I1) + FIELD2**2*H2E(I2,I1)/GAMMA
   92 WRITE(6,113) I2, (ENRG1E(I2,I1), I1=1,3), (ENRG2E(I2,I1), I1=1,3)
      DO 81 I1 = 1,3
      SUM1E(I1) = 0.0
      SUM2E(I1) = 0.0
      DO 80 I2 = 2,14
      SUM1E(I1) = SUM1E(I1) + ENRG1E(I2,I1)
   80 SUM2E(I1) = SUM2E(I1) + ENRG2E(I2,I1)
      SUM1E(I1) = 4.0*SUM1E(I1) - 2.0*(ENRG1E(2,I1) + ENRG1E(3,I1) +
     1 ENRG1E(5,I1) + ENRG1E(6,I1) + ENRG1E(12,I1))
      SUM2E(I1) = 4.0*SUM2E(I1) - 2.0*(ENRG2E(2,I1) + ENRG2E(3,I1) +
     1 ENRG2E(5,I1) + ENRG2E(6,I1) + ENRG2E(12,I1))
      SUM1EN(I1) = SUM1E(I1) - 8.0*(ENRG1E(9,I1) + ENRG1E(10,I1) +
     1 ENRG1E(11,I1) + ENRG1E(14,I1))
   81 SUM2EN(I1) = SUM2E(I1) - 8.0*(ENRG2E(9,I1) + ENRG2E(10,I1) +
     1 ENRG2E(11,I1) + ENRG2E(14,I1))
      WRITE(6,114) SUM1E, SUM2E
      WRITE(6,115) SUM1EN, SUM2EN
      DO 13 I2 = 2,14
      DO 14 I1 = 1,3
      EENRG1(I2,I1) = ENRG1E(I2,I1)/CM
   14 EENRG2(I2,I1) = ENRG2E(I2,I1)/CM
   13 WRITE(6,113) I2, (EENRG1(I2,I1), I1=1,3), (EENRG2(I2,I1), I1=1,3)
      DO 15 I1 = 1,3
      ESUM1(I1) = SUM1E(I1)/CM
```

```
      ESUM2(I1) = SUM2E(I1)/CM
      ESUM1N(I1) = SUM1EN(I1)/CM
 15   ESUM2N(I1) = SUM2EN(I1)/CM
      WRITE(6,411) ESUM1, ESUM2
      WRITE(6,511) ESUM1N, ESUM2N
      STOP
      END
```

THIS SUBROUTINE FINDS THE VALUES OF PARAMETERS NEEDED IN THE CALCULATION OF THE OVERLAP INTEGRALS, FROM THE VALUES OF THE SLATER SCF PARAMETERS AND ORBITAL EXPONENTS, A AND ALPHA.

```
      SUBROUTINE PRMTRS (ALPHA, A, C1, D1, A1, ALPHA1)
      DIMENSION ALPHA(4), A(4), C1(6), D1(6), A1(6), ALPHA1(6)
      DOUBLE PRECISION ALPHA, ALPHA1, A, A1
      J = 1
      DO 11 K = 1,3
      K1 = K+1
      DO 11 L = K1,4
      C1(J) = (ALPHA(K) + ALPHA(L))/2.0
      D1(J) = (ALPHA(L) - ALPHA(K))/2.0
      A1(J) = A(K)*A(L)
      ALPHA1(J) = (ALPHA(K)*ALPHA(L))**2.5
 11   J = J+1
      RETURN
      END
```

THIS SUBROUTINE PRINTS THE OUTPUT OF A MXN MATRIX

```
      SUBROUTINE OUTPT1 (A, M, N)
      DIMENSION A(M,N)
      DOUBLE PRECISION A
      KITE = 0
 20   LOW = KITE + 1
      KITE = KITE + 10
      KITE = MIN0 (KITE, N)
      WRITE(6,19) (I, I = LOW,KITE)
 19   FORMAT (1H0, 9X, I2, 9(11X, I2)//)
      DO 32 I = 1,M
 32   WRITE(6,18) I, (A(I,J), J = LOW,KITE)
 18   FORMAT (1H , I2, 10(1PE13.4))
      IF (N - KITE) 40, 40, 20
 40   RETURN
      END
```

THIS SUBROUTINE CALCULATES DELTA E FOR DIFFERENT VALUES OF A AND B.

```
      SUBROUTINE DLE(A, B, MI, DELEN)
      DIMENSION MI(14)
      DOUBLE PRECISION DELEN
      INTEGER A, B
      REAL MI
      DELEN = MI(A) - MI(B)
      RETURN
      END
```

THIS SUBROUTINE FINDS THE COORDINATES, AND NORMAL TO THE PLANE OF MOLECULE B, FROM THE COORDINATES AND NORMAL TO THE PLANE OF MOLECULE A. IT CONVERTS THESE FROM ANGSTROMS TO ATOMIC UNITS. IT ALSO FINDS THE DOT PRODUCT OF N1 AND N2.

```
      SUBROUTINE COORD(RA, RB, N1, N2, N1N2, RA1, RB2)
      DIMENSION RA(14,3),RB(14,14,3),N1(3),N2(3),RA1(14,3),RB2(14,14,3)
      DOUBLE PRECISION RA,RB,N1,N2,N1N2,RA1,RB2,A,B,C,C1,D,BETA
      A=8.561
      B=6.036
      C1=11.163
      BETA = 2.17642577D0
      C = C1*DSIN(BETA)
      D = C1*DCOS(BETA)
      DO 100 J=1,14
      RB2(2,J,1) = RA1(J,1) + D
      RB2(2,J,2) = RA1(J,2)
      RB2(2,J,3) = RA1(J,3) + C
      RB2(3,J,1) = RA1(J,1)
      RB2(3,J,2) = RA1(J,2) + B
      RB2(3,J,3) = RA1(J,3)
      RB2(4,J,1) = RA1(J,1) + D
      RB2(4,J,2) = RA1(J,2) + B
      RB2(4,J,3) = RA1(J,3) + C
      RB2(5,J,1) = RA1(J,1) + A
      RB2(5,J,2) = RA1(J,2)
      RB2(5,J,3) = RA1(J,3)
      RB2(6,J,1) = RA1(J,1) + A + D
      RB2(6,J,2) = RA1(J,2)
      RB2(6,J,3) = RA1(J,3) + C
      RB2(7,J,1) = RA1(J,1) + A
      RB2(7,J,2) = RA1(J,2) + B
      RB2(7,J,3) = RA1(J,3)
      RB2(8,J,1) = RA1(J,1) + A + D
      RB2(8,J,2) = RA1(J,2) + B
      RB2(8,J,3) = RA1(J,3) + C
      RB2(9,J,1) = RA1(J,1) + A/2.0
      RB2(9,J,2) =-RA1(J,2) + B/2.0
      RB2(9,J,3) = RA1(J,3)
      RB2(10,J,1) = RA1(J,1) + A/2.0 + D
      RB2(10,J,2) =-RA1(J,2) + B/2.0
      RB2(10,J,3) = RA1(J,3) + C
      RB2(11,J,1) = RA1(J,1) - A/2.0 + D
      RB2(11,J,2) =-RA1(J,2) + B/2.0
      RB2(11,J,3) = RA1(J,3) + C
      RB2(12,J,1) = RA1(J,1) - A + D
      RB2(12,J,2) = RA1(J,2)
      RB2(12,J,3) = RA1(J,3) + C
      RB2(13,J,1) = RA1(J,1) - A + D
      RB2(13,J,2) = RA1(J,2) + B
      RB2(13,J,3) = RA1(J,3) + C
      RB2(14,J,1) = RA1(J,1) + A/2.0
      RB2(14,J,2) =-RA1(J,2) + B*3.0/2.0
  100 RB2(14,J,3) = RA1(J,3)
      DO 200 I1 = 1,3
      DO 200 J=1,14
      RA(J,I1) = RA1(J,I1)/0.529167
      DO 200 I = 2,14
  200 RB(I,J,I1) = RB2(I,J,I1)/0.529167
      N2(1) = N1(1)
      N2(2) = -N1(2)
      N2(3) = N1(3)
      N1N2 = N1(1)*N2(1) + N1(2)*N2(2) + N1(3)*N2(3)
      RETURN
      END
```

THIS SUBROUTINE FINDS THE VALUE OF THE OVERLAP INTEGRAL BETWEEN TWO CARBON 2P-PI ATOMIC ORBITALS, GIVEN THEIR COORDINATES AND RELATIVE CONFIGURATIONS

```
      SUBROUTINE OVRLP(S, R1, R2, N)
      COMMON N1(3), N2(3), ALPHA(4), A(4), ALPHA1(6), A1(6), C1(6),
     1 D1(6), N1N2
      DIMENSION R1(3), R2(3), ALPHAR(4), C(6), D(6), R12(3)
      DOUBLE PRECISION ALPHA, ALPHA1, A, A1, C, D, ALPHAR, SUM1, SUM2,
     1 SUM3, SUM4, N1R, N2R, N1, N2, R12, SUMR, R, N1N2, S,OVRLPS,OVRLPC
      N1R = 0.0
      N2R = 0.0
      SUMR = 0.0
      DO 10 I1 = 1,3
      R12(I1) = (R1(I1) - R2(I1))
      N1R = N1R + N1(I1)*R12(I1)
      IF (N .EQ. 1) GO TO 10
      N2R = N2R + N2(I1)*R12(I1)
   10 SUMR = SUMR + R12(I1)**2
      R = DSQRT(SUMR)
      IF (N .EQ. 1) N2R = N1R
      IF (N .EQ. 1) N1N2 = 1.0D0
      SUM1 = 0.0
      SUM3 = 0.0
      DO 100 I = 1,4
      ALPHAR(I) = ALPHA(I)*R
      IF (ALPHAR(I) .GT. 170D0) GO TO 100
      SUM3 = SUM3 + (A(I)**2)*DEXP(-ALPHAR(I))*(1.0 + ALPHAR(I) +
     1 ALPHAR(I)**2/5.0 - 2.0*ALPHAR(I)**3/15.0 - ALPHAR(I)**4/15.0)
      SUM1 = SUM1 + (A(I)**2)*DEXP(-ALPHAR(I))*(ALPHAR(I)**3/15.0 +
     1 2.0*ALPHAR(I)**2/5.0 + ALPHAR(I) + 1.0)
  100 CONTINUE
      SUM2 = 0.0
      SUM4 = 0.0
      DO 200 J = 1,6
      C(J) = C1(J)*R
      IF (C(J) .GT. 155D0) GO TO 200
      D(J) = D1(J)*R
      SUM4=SUM4+A1(J)*ALPHA1(J)*DEXP(-C(J))*((DEXP(D(J))+DEXP(-D(J)))*
     1(-1.0/D(J)**2*(1.0/(3.0*C(J)**3)+1.0/C(J)**4+1.0/C(J)**5)+
     21.0/D(J)**4*(1.0/(2.0*C(J))+1.0/C(J)**2+1.0/C(J)**3))+(DEXP(D(J))-
     3DEXP(-D(J)))*(1.0/D(J)*(1.0/(6.0*C(J)**3)+1.0/(2.0*C(J)**4)+1.0/
     4(2.0*C(J)**5))+1.0/D(J)**3*(-1.0/(6.0*C(J))-1.0/(3.0*C(J)**2)+1.0/
     5C(J)**4+1.0/C(J)**5)-1.0/D(J)**5*(1.0/(2.0*C(J))+1.0/C(J)**2+1.0/
     6C(J)**3)))
      SUM2=SUM2+A1(J)*ALPHA1(J)*DEXP(-C(J))*((DEXP(D(J))+DEXP(-D(J)))*
     1(1.0/D(J)**2*(1.0/(3.0*C(J)**3)+1.0/C(J)**4+1.0/C(J)**5)- 1.0/
     2D(J)**4*(1.0/C(J)**2+1.0/C(J)**3))+(DEXP(D(J))-DEXP(-D(J)))*(1.0/
     3D(J)**3*(1.0/(3.0*C(J)**2)-1.0/C(J)**4-1.0/C(J)**5)+1.0/D(J)**5*
     4(1.0/C(J)**2+1.0/C(J)**3)))
  200 CONTINUE
      SUM2 = 3.0*R**5*SUM2
      SUM4 = 6.0*R**5*SUM4
      OVRLPC = (N1N2 - N1R*N2R/SUMR)*(SUM1 + SUM2)
      OVRLPS = (N1R*N2R/SUMR)*(SUM3 + SUM4)
      S = OVRLPS + OVRLPC
      RETURN
      END
```

```
THE PURPOSE OF THIS PROGRAM IS TO FIND THE INTERMOLECULAR RESONANCE INTEGRAL
BETWEEN TWO WAVE FUNCTIONS ON THE SAME ATOM AND THE POTENTIAL ON A DIFFERENT
ATOM(TWO-CENTERS).  THIS WAS DONE ANALYTICALLY USING ELLIPTICAL COORDINATES.
      DIMENSION C7(14), C8(14), C72(14), C82(14), N1(3), RA1(14,3),
     1 RB2(14,14,3), RA(14,3), RB(14,14,3), R1(3), R2(3), R12(3),
     2 RSAT(14), RSHB(14), RSEB(14)
      COMMON A(4), ALF(4)
      REAL N1, NR, INT1, INT2, INT3, INT4
      READ(5,101) C7, C8, A, ALF, N1, ((RA1(J,I1), I1=1,3), J=1,14)
  101 FORMAT (4(7F9.6/), 4F7.5, 4F6.4/(3F7.4))
      WRITE(6,102)
  102 FORMAT (1H1, 45HTWO CENTER INTERMOLECULAR RESONANCE INTEGRALS/
     1 4H MOL, 5X, 9HHOLE BAND, 5X, 13HELECTRON BAND)
      SUMKL=0.0
      DO 99 K=1,4
      DO 99 L=1,4
   99 SUMKL=SUMKL+A(K)*A(L)*(ALF(K)*ALF(L))**2.5/(.5*(ALF(K)+ALF(L)))**5
      DO 100 I=1,14
      C72(I)=C7(I)*C7(I)
  100 C82(I)=C8(I)*C8(I)
      CALL COORD(RA, RB, RA1, RB2)
      DO 500 I2=2,14
      RSHB(I2)=0.0
      RSEB(I2)=0.0
      DO 400 I=1,14
      RSAT(I)=0.0
      DO 300 J=1,14
      NR=0.0
      SUMR=0.0
      DO 200 I1=1,3
      R1(I1)=RA(I,I1)
      R2(I1)=RB(I2,J,I1)
      R12(I1)=(R1(I1)-R2(I1))
      NR=NR+N1(I1)*R12(I1)
  200 SUMR=SUMR+R12(I1)**2
      R=SQRT(SUMR)
      IF (R .GT. 18.89763) GO TO 300
      SUM1=0.0
      SUM2=0.0
      DO 10 K=1,4
      CALL INT(K,K,K,K,R,INT1,INT2)
      SUM1=SUM1+INT1
   10 SUM2=SUM2+INT2
      SUM3=0.0
      SUM4=0.0
      DO 20 L=2,4
      LM=L-1
      DO 20 K=1,LM
      CALL INT(K,L,K,L,R,INT1,INT2)
      SUM3=SUM3+INT1
   20 SUM4=SUM4+INT2
      SUM5=0.0
      SUM6=0.0
      DO 30 M=2,4
      MM=M-1
      DO 30 K=1,MM
```

```
      CALL INT(K,K,M,M,R,INT3,INT4)
      SUM5=SUM5+INT3
   30 SUM6=SUM6+INT4
      SUM7=0.0
      SUM8=0.0
      DO 40 L=2,4
      LM=L-1
      DO 40 K=1,LM
      DO 40 M=1,4
      CALL INT(K,L,M,M,R,INT3,INT4)
      SUM7=SUM7+INT3
   40 SUM8=SUM8+INT4
      SUM9=0.0
      SUM10=0.0
      DO 50 L=2,4
      LM=L-1
      DO 50 K=1,LM
      DO 50 N=3,4
      NM=N-1
      DO 50 M=1,NM
      IF ((10*K+L) .GE. (10*M+N)) GO TO 50
      CALL INT(K,L,M,N,R,INT3,INT4)
      SUM9=SUM9+INT3
      SUM10=SUM10+INT4
   50 CONTINUE
      RSAT(I)=RSAT(I)+(NR/R)**2*(SUM1+4.0*SUM3+SUM5+2.0*SUM7+4.0*SUM9)+
     1(1.0-(NR/R)**2)*(SUM2+4.0*SUM4+SUM6+2.0*SUM8+4.0*SUM10)
  300 CONTINUE
      RSHB(I2)=RSHB(I2)-108.840/SUMKL*C72(I)*RSAT(I)
  400 RSEB(I2)=RSEB(I2)-108.840/SUMKL*C82(I)*RSAT(I)
  500 WRITE(6,103) I2, RSHB(I2), RSEB(I2)
  103 FORMAT (1H , I2, 5X, 1PE11.4, 5X, E11.4)
      STOP
      END
```

COMPARE THE PREVIOUS PROGRAM (P. 86), FOR SUBROUTINE COORD.

```
THIS SUBROUTINE FINDS A TERM OF THE RESONANCE INTEGRAL BETWEEN THE WAVE
FUNCTION ON MOLECULE 1, ATOM I, AND THE POTENTIAL ON MOLECULE I2, ATOM J
      SUBROUTINE INT(K,L,M,N,R,X,Y)
      COMMON A(4), ALF(4)
      DIMENSION B(4,4)
      REAL INT1, INT2, INT3, INT4
      B(K,L)=0.5*(ALF(K)+ALF(L))
      B(M,N)=0.5*(ALF(M)+ALF(N))
      G=(B(K,L)+B(M,N))*R
      IF (G .GT. 170.0) GO TO 2
      G1=(1.0/G+1.0/G**2)
      G2=(1.0/G+2.0/G**2+2.0/G**3)
      G3=(1.0/G+3.0/G**2+6.0/G**3+6.0/G**4)
      G4=(1.0/G+4.0/G**2+12.0/G**3+24.0/G**4+24.0/G**5)
      G5=(1.0/G+5.0/G**2+20.0/G**3+60.0/G**4+120.0/G**5+120.0/G**6)
      G6=(1.0/G+6.0/G**2+30.0/G**3+120.0/G**4+360.0/G**5+720.0/G**6+
     1720.0/G**7)
      IF (K .EQ. M .AND. L .EQ. N) GO TO 1
      U=(B(K,L)-B(M,N))*R
      IF (ABS(U) .GT. 170.0) GO TO 2
      U0=EXP(U)/U-EXP(-U)/U
      U2=EXP(U)*(1.0/U-2.0/U**2+2.0/U**3)-EXP(-U)*(1.0/U+2.0/U**2+
     12.0/U**3)
      U4=EXP(U)*(1.0/U-4.0/U**2+12.0/U**3-24.0/U**4+24.0/U**5)-EXP(-U)*
     1(1.0/U+4.0/U**2+12.0/U**3+24.0/U**4+24.0/U**5)
      U6=EXP(U)*(1.0/U-6.0/U**2+30.0/U**3-120.0/U**4+360.0/U**5-
     1 720.0/U**6+720.0/U**7)-EXP(-U)*(1.0/U+6.0/U**2+30.0/U**3+
     2 120.0/U**4+360.0/U**5+720.0/U**6+720.0/U**7)
      INT3=A(K)*A(L)*A(M)*A(N)*(ALF(K)*ALF(L)*ALF(M)*ALF(N))**2.5/
     1B(M,N)**5*(B(M,N)**3*R**7/96.0*(G6*U2+G4*(U0 -4.0*U2)+G2*(4.0*U4-
     2U6))+B(M,N)**2*R**6/16.0*(G5*U2+G3*(U0 -2.0*U2-U4)-G1*(U2-2.0*U4))
     3+3.0*B(M,N)*R**5/16.0*(G4*U2+G2*(U0-U4)-U2/G)+R**4/4.0*(G3*U2+G1*
     4(U0 +2.0*U2)))*EXP(-G)
      INT4=A(K)*A(L)*A(M)*A(N)*(ALF(K)*ALF(L)*ALF(M)*ALF(N))**2.5/
     1B(M,N)**5*(B(M,N)**3*R**7/96.0*(G6*(U0 -U2)-G4*(U0 -U2)-G2*(U4-U6)
     2+(U4-U6)/G)+B(M,N)**2*R**6/16.*(G5*(U0-U2)-G3*(U0-U4)-G1*(U2-U4))+
     33.0*B(M,N)*R**5/16.0*(G4*(U0-U2)-G2*(U0-U4)+(U2-U4)/G)+R**4/4.*(G3
     4*(U0-U2)-G1*(U0 -U2)))*EXP(-G)
      X=INT3
      Y=INT4
      RETURN
    1 INT1=(A(K)*A(L))**2*(ALF(K)*ALF(L)/B(M,N))**5*(B(M,N)**3*R**7/96.0
     1*(G6/3.0-G4/3.0+23.0*G2/35.-.2/G)+B(M,N)**2*R**6/16.0*(G5/3.0+2.0*
     2G3/15.0+G1/15.0)+3.0*B(M,N)*R**5/16.0*(G4/3.0+4.*G2/5.-1./(3.*G))+
     3R**4/4.0*(G3/3.0+5.0*G1/3.0))*EXP(-G)
      INT2=(A(K)*A(L))**2*(ALF(K)*ALF(L)/B(M,N))**5*(B(M,N)**3*R**7/96.0
     1*(2.0*G6/3.0-2.0*G4/3.0-2.*G2/35.+2./(35.*G))+B(M,N)**2*R**6/16.0*
     2(2.0*G5/3.0-4.0*G3/5.0-2.0*G1/15.0)+3.0*B(M,N)*R**5/16.0*(2.0*G4/
     33.0-4.*G2/5.+2./(15.*G))+R**4/4.0*(2.0*G3/3.0-2.0*G1/3.0))*EXP(-G)
      X=INT1
      Y=INT2
      RETURN
    2 X=0.0
      Y=0.0
      RETURN
      END
```

```
      PROGRAM RESINT(INPUT.OUTPUT.TAPE5=INPUT.TAPE6=OUTPUT)
THIS PROGRAM FINDS THE 3-CENTER INTEGRAL BETWEEN TWO WAVEFUNCTIONS ON
NEIGHBORING ATOMS. AND THE POTENTIAL ON A THIRD ATOM.
LIKEWISE. FOR NEXT NEAREST NEIGHBOR ATOMS.
      DIMENSION C7(24). C8(24). N1(3). RA1(16.3). RB2(16.16.3).RA(32.3).
    1 RB(16.16.3). R1(3). R2(3). R12(3). R3(3). R(20). BR(20). Y1(20).
    2 B1(20). Y2(20). B2(20). Q(14). INTH(14). INTE(14). R123(3).ALF(4)
    3 .HINT(16.2). EINT(16.2). DIST(14)
      COMMON/CD/ RA. SPACEX. RB. SPACEY. RA1. SPACEZ. RB2
      COMMON/CN/ C7. C8
      COMMON/OR/ R1.SPACE4. R2. SPACE5. R3. SPACE6. R12
      COMMON/FOR/ U(3). SPACE7. V(3). SPACE8. W(3)
      COMMON/APX/ N. SPACEA. R. SPACEB. BR. SPACEC. Y1. SPACED. B1.
    1 SPACEE. Y2. SPACEF. B2
      COMMON/FST/ A(4). SPACE1. SALF(4). SPACE2. SUMKL. SPACE3. N1
      EXTERNAL RIRJVM
      REAL N1. INTH. INTE
      READ(5.101) (C7(K). K=1.14). (C8(L). L=1.14).A. ALF. N1.
    1 ((RA1(J.I1).I1=1.3).J=1.14). N. (R(I). BR(I). Y1(I). B1(I).
    2 Y2(I). B2(I). I=1.N)
  101 FORMAT (4(7F9.6/). 4F7.5. 4F6.4/ 15(3F7.4/). I4/ (6F11.8))
      SUMKL = 0.0
      DO 99 K=1.4
      DO 99 L=1.4
   99 SUMKL = SUMKL + A(K)*A(L)*(ALF(K)*ALF(L))**2.5/(0.5*(ALF(K) +
    1 ALF(L)))**5
      C7(15) = C7(1)
      C7(16) = C7(8)
      C8(15) = C8(1)
      C8(16) = C8(8)
      CALL COORD
      DO 500 K = 1.2
      IF (K .EQ. 2) CALL CONNN (RA)
      K2 = 16 + K*(K*K-1)
      WRITE(6.105)
  105 FORMAT(1H1)
      DO 500 I2=2.14
      HIN = 0.0
      EIN = 0.0
      IF (K .EQ. 2) GO TO 19
      INTH(I2) = 0.0
      INTE(I2) = 0.0
   19 DO 400 II = 1.K2
      I = II
      J = I + K
      IF (K .EQ. 2) GO TO 21
      IF (I .EQ. 15) J = 6
      IF (I.EQ.16) J=13
   21 IF (I .EQ. 21) I = 1
      QQ=0.0
      DO 300 M=1.14
      SUMR=0.0
      DO 100 I1=1.3
      R1(I1)=RA (I.I1)
      R2(I1)=RA(J.I1)
      R3(I1)=RB(I2.M.I1)
```

```
      R12(I1)=(R1(I1)+R2(I1))/2.0
      R123(I1)=R3(I1)-R12(I1)
  100 SUMR=SUMR+R123(I1)*R123(I1)
      DIST(M) = SQRT(SUMR)
      IF (K .EQ. 2) GO TO 96
      IF (DIST(M) .GT. 12.28346) GO TO 299
      GO TO 95
   96 IF (DIST(M) .GT. 9.92125) GO TO 299
   95 DO 98 IA = 1.4
   98 SALF(IA) = ALF(IA)*DIST(M)
      DO 97 I1 = 1.3
      R1(I1) = R1(I1)/DIST(M)
      R2(I1) = R2(I1)/DIST(M)
      R3(I1) = R3(I1)/DIST(M)
   97 R12(I1) = R12(I1)/DIST(M)
      CALL ORIGIN
      Q(M)=APPROX(RIRJVM)
      GO TO 298
  299 Q(M) = 0.0
  298 QQ = QQ + Q(M)/DIST(M)
  300 CONTINUE
      WRITE(6.102) I. J. QQ. (M. Q(M). DIST(M). M=1.14)
  102 FORMAT(1H0. 3HI =. I3. 4H J =. I3. 5H QQ =. 1PE16.8//3H0 M. 8X.
     1 1HQ. 12X. 8HDISTANCE//(1H . I2. 2E16.8))
      HIN = HIN + C7(I)*C7(J)*QQ
  400 EIN = EIN + C8(I)*C8(J)*QQ
      HINT(I2.K) = -HIN*8.6612
      EINT(I2.K) = -EIN*8.6612
      INTH(I2) = INTH(I2) + HINT(I2.K)
  500 INTE(I2) = INTE(I2) + EINT(I2.K)
      WRITE(6.103)
  103 FORMAT(1H1. &MOL&. 29X. &HOLE BAND&. 32X. &ELECTRON BAND&/1H .
     1 13X. &N-N&. 15X. &N-N-N&. 14X. &TOTAL&. 20X. &N-N&. 15X. &N-N-N&.
     2 14X. &TOTAL&//)
      WRITE(6.104) (I2. (HINT(I2.K). K=1.2). INTH(I2). (EINT(I2.K).
     1 K=1.2). INTE(I2). I2=2.14)
  104 FORMAT(1H . I3. 1P3E19.8. 5X. 3E19.8)
      STOP
      END
```

THE SUBROUTINE COORD IS A MODIFICATION OF THE ONE ON P. 86
WITH THE FOLLOWING ADDITION:

```
      DO 201 I1=1.3
      RA (15.I1) = RA (1.I1)
  201 RA (16.I1) = RA (8.I1)
```

```
      SUBROUTINE CONNN (RA)
THIS SUBROUTINE, FINDS THE VALUES OF THE COEFFICIENTS AND COORDINATES, OF THE
NEXT NEAREST NEIGHBOR ATOMS OF MOLECULE 1.
      DIMENSION C7(24), C8(24), RA(32,3)
      COMMON/CN/ C7, C8
      C7(15) = C7(1)
      C7(16) = C7(2)
      C7(17) = C7(7)
      C7(18) = C7(6)
      C7(19) = C7(13)
      C7(20) = C7(14)
      C7(21) = C7(9)
      C7(22) = C7(8)
      C7(23) = C7(5)
      C7(24) = C7(12)
      C8(15) = C8(1)
      C8(16) = C8(2)
      C8(17) = C8(7)
      C8(18) = C8(6)
      C8(19) = C8(13)
      C8(20) = C8(14)
      C8(21) = C8(9)
      C8(22) = C8(8)
      C8(23) = C8(5)
      C8(24) = C8(12)
      DO 201 I1 = 1,3
      RA(15,I1) = RA(1,I1)
      RA(16,I1) = RA(2,I1)
      RA(17,I1) = RA(7,I1)
      RA(18,I1) = RA(6,I1)
      RA(19,I1) = RA(13,I1)
      RA(20,I1) = RA(14,I1)
      RA(21,I1) = RA(9,I1)
      RA(22,I1) = RA(8,I1)
      RA(23,I1) = RA(5,I1)
  201 RA(24,I1) = RA(12,I1)
      RETURN
      END

      SUBROUTINE ORIGIN
THIS SUBROUTINE FINDS THE ORIGIN OF THE SPHERICAL COORDINATE SYSTEM BY TAKING
THE MIDPOINT OF THE TWO NEAREST NEIGHBOR ATOMS, AND THEN THE MIDPOINT OF THE
LINE BETWEEN THAT POINT AND THE ATOM ON WHICH THE POTENTIAL IS LOCATED.
      DIMENSION R1(3), R2(3), R3(3), R4(3), R12(3)
      COMMON/OR/ R1,SPACE4, R2, SPACE5, R3, SPACE6, R12
      COMMON/FOR/ U(3), SPACE7, V(3), SPACE8, W(3)
      DO 77 I1=1,3
      R4(I1) = (R12(I1) + R3(I1))/2.0
      U(I1) = R1(I1) - R4(I1)
      V(I1) = R2(I1) - R4(I1)
   77 W(I1) = R3(I1) - R4(I1)
      RETURN
      END
```

```
      FUNCTION RIRJVM(X1. Y. Z)
THIS FUNCTION REPRESENTS THE INTEGRAL TO BE SOLVED.
      COMMON/FOR/ U(3). SPACE7. V(3). SPACE8. W(3)
      COMMON/FST/ A(4). SPACE1.  ALF(4). SPACE2. SUMKL. SPACE3. N1
      DIMENSION BETA(4.4). N1(3). X(3)
      REAL NA. NB. N1
      X(1) = X1
      X(2) = Y
      X(3) = Z
      NA = 0.0
      NB = 0.0
      AX = 0.0
      BX = 0.0
      CX = 0.0
      DO 10 I1 = 1.3
      NA = NA + N1(I1)*(U(I1)-X(I1))
      NB = NB + N1(I1)*(V(I1)-X(I1))
      AX = AX + (U(I1)-X(I1))*(U(I1)-X(I1))
      BX = BX + (V(I1)-X(I1))*(V(I1)-X(I1))
   10 CX = CX + (W(I1)-X(I1))*(W(I1)-X(I1))
      AX = SQRT(AX)
      BX = SQRT(BX)
      CX = SQRT(CX)
      RRV1 = 0.0
      RRV2 = 0.0
      RRV3 = 0.0
      RRV4 = 0.0
      DO 21 I = 1.4
      DO 21 K = 1.4
      ARG = ALF(I)*(AX + BX) + 2.0*ALF(K)*CX
      IF (ARG .GT. 30.0) GO TO 21
      RRV1 = RRV1 + A(I)*A(I)*A(K)*A(K)*ALF(I)**5/SUMKL*EXP(-ARG)*
     1(4.0/3.0*ALF(K)**3*CX*CX + 4.0*ALF(K)*ALF(K)*CX + 6.0*ALF(K) +
     2 4.0/CX)
   21 CONTINUE
      DO 22 I = 1.4
      DO 22 L = 2.4
      LL = L-1
      DO 22 K = 1.LL
      BETA(K.L) = (ALF(K) + ALF(L))/2.0
      ARG1 = ALF(I)*(AX + BX) + 2.0*BETA(K.L)*CX
      IF (ARG1 .GT. 30.0) GO TO 221
      RRV2 = RRV2 + A(I)*A(I)*A(K)*A(L)*(ALF(I)*ALF(I)*ALF(K)*ALF(L))**
     1 2.5/BETA(K.L)**5/SUMKL*EXP(-ARG1)*(4.0/3.0*BETA(K.L)**3*CX*CX +
     2 4.0*BETA(K.L)*BETA(K.L)*CX + 6.0*BETA(K.L) + 4.0/CX)
  221 ARG2 = ALF(K)*AX + ALF(L)*BX + 2.0*ALF(I)*CX
      ARG3 = ALF(L)*AX + ALF(K)*BX + 2.0*ALF(I)*CX
      E2 = 0.0
      E3 = 0.0
      IF (ARG2 .GT. 30.0) GO TO 222
      E2 = EXP(-ARG2)
  222 IF (ARG3 .GT. 30.0) GO TO 223
      E3 = EXP(-ARG3)
  223 IF (E2 .EQ. 0.0 .AND. E3 .EQ. 0.0) GO TO 22
      RRV3 = RRV3 + A(K)*A(L)*A(I)*A(I)*(ALF(K)*ALF(L))**2.5/SUMKL*
```

```
     1 (E2 + E3)*(4.0/3.0*ALF(I)**3*CX*CX + 4.0*ALF(I)*ALF(I)*CX +
     2 6.0*ALF(I) + 4.0/CX)
 22   CONTINUE
      DO 23 J = 2,4
      JJ = J-1
      DO 23 I = 1,JJ
      DO 23 L = 2,4
      LL = L-1
      DO 23 K = 1,LL
      BETA(K,L) = (ALF(K) + ALF(L))/2.0
      ARG4 = ALF(I)*AX + ALF(J)*BX + 2.0*BETA(K,L)*CX
      ARG5 = ALF(J)*AX + ALF(I)*BX + 2.0*BETA(K,L)*CX
      E4 = 0.0
      E5 = 0.0
      IF (ARG4 .GT. 30.0) GO TO 231
      E4 = EXP(-ARG4)
231   IF (ARG5 .GT. 30.0) GO TO 232
      E5 = EXP(-ARG5)
232   IF (E4 .EQ. 0.0 .AND. E5 .EQ. 0.0) GO TO 23
      RRV4 = RRV4 + A(I)*A(J)*A(K)*A(L)*(ALF(I)*ALF(J)*ALF(K)*ALF(L))**
     1 2.5/BETA(K,L)**5/SUMKL*(E4 + E5)*(4.0/3.0*BETA(K,L)**3*CX*CX +
     2 4.0*BETA(K,L)*BETA(K,L)*CX + 6.0*BETA(K,L) + 4.0/CX)
 23   CONTINUE
      RIRJVM = NA*NB*(RRV1 + 2.0*RRV2 + RRV3 + 2.0*RRV4)
      RETURN
      END

      FUNCTION APPROX(FF)
THIS FUNCTION APPROXIMATES THE INTEGRAL OF THE FUNCTION FF OVER THE 3-DIMEN-
SIONAL SPHERE USING THE PRODUCT OF THE 3 ONE DIMENSIONAL, N-POINT, QUADRATURE
FORMULAS CONTAINED IN THE ARRAYS R, BR, Y1, B1, Y2, B2.
      DIMENSION R(20), BR(20), Y1(20), B1(20), Y2(20), B2(20)
      COMMON/APX/ N, SPACEA, R, SPACEB, BR, SPACEC, Y1, SPACED, B1,
     1 SPACEE, Y2, SPACEF, B2
      Q = 0.0
      DO 2 I=1,N
      DO 2 J=1,N
      DO 2 K=1,N
      B=BR(I)*B1(J)*B2(K)
      X=R(I)*SQRT(1.0-Y2(K)*Y2(K))*SQRT(1.0-Y1(J)*Y1(J))
      Y=R(I)*Y1(J)*SQRT(1.0-Y2(K)*Y2(K))
      Z=R(I)*Y2(K)
    2 Q=Q+B*FF(X,Y,Z)
      APPROX=Q
      RETURN
      END
```

```
THIS PROGRAM CALCULATES THE ELECTRON AND HOLE SURFACE BANDS OF
ANTHRACENE AND NAPHTHALENE IN THE AC PLANE

      DIMENSION A(4,3), B(4,3), C(4), A1(4,3), B1(4,3), ANG(37), ROOT(3)
     1, AK(3), BK(3), E1(3,37), E2(3,37), E3(3,37), E4(3,37),
     2 KSI1(3,37), KSI2(3,37), D(4,3), D1(4,3), DK(3)
      REAL KS1, KS2, KS3, KS4, KSI1, KSI2
READ IN THE VALUES OF THE RESONANCE INTEGRALS FOR VARIOUS GROUPS OF MOLECULES
      READ(5,101) (C(I), I=1,4), ((A(I,J), A1(I,J), I=1,4), J=1,3),
     1 ((B(I,J), B1(I,J), I=1,4), J=1,3), ((D(I,J),D1(I,J),I=1,4),J=1,3)
  101 FORMAT (4F7.2/(8F7.2))
PRINT OUT INPUT DATA
      WRITE(6,107)
  107 FORMAT(1H1,33X,'ANTHRACENE',19X,'NAPHTHALENE'/31X,'HOLE',5X,
     1'ELECTRON',12X,'HOLE',5X,'ELECTRON')
      WRITE(6,108)((A(I,J),I=1,4),(A1(I,J),I=1,4),(B(I,J),I=1,4),
     1 (B1(I,J),I=1,4),J=1,3), C,((D(I,J),I=1,4),(D1(I,J),I=1,4),J=1,3)
  108 FORMAT('0A(A)=E3+2E4',17X,2(F7.2,5X),2(5X,F7.2)/ ' A1(A)=2(E7+E8+E
     113)',10X,2(F7.2,5X),2(5X,F7.2)/' B(A)',24X,2(F7.2,5X),2(5X,F7.2)/
     2' B1(A)=E9+E10+E11',12X,2(F7.2,5X),2(5X,F7.2)//' A(B)=E3+2(E4+E7+E
     38+E13)',5X,2(F7.2,5X),2(5X,F7.2)/' A1(B)',23X,2(F7.2,5X),2(5X,
     4F7.2)/' B(B)=E9+E10+E11',13X,2(F7.2,5X),2(5X,F7.2)/' B1(B)',23X,
     52(F7.2,5X),2(5X,F7.2)//' A(C)=E3+2E7',17X,2(F7.2,5X),2(5X,F7.2)/
     6' A1(C)=2(E4+E8+E13)',10X,2(F7.2,5X),2(5X,F7.2)/' B(C)=E9',21X,
     72(F7.2,5X),2(5X,F7.2)/' B1(C)=E10+E11',15X,2(F7.2,5X),2(5X,F7.2)//
     8' C=ALPHA-ALPHA''',14X,2(F7.2,5X),2(5X,F7.2)//' D(A)=2E2',20X,
     92(F7.2,5X),2(5X,F7.2)/' D1(A)=2(E5+E5+E12)',10X,2(F7.2,5X),2(5X,
     1F7.2)//' D(B)=2(E2+E5+E6+E12)',8X,2(F7.2,5X),2(5X,F7.2)/' D1(B)',
     123X,2(F7.2,5X),2(5X,F7.2)//' D(C)=2E5',20X,2(F7.2,5X),2(5X,F7.2)/
     2' D1(C)=2(E2+E6+E12)',10X,2(F7.2,5X),2(5X,F7.2)/)
      PI = 3.141593
CALCULATE THE ENERGY OF EACH OF THE FOUR DIFFERENT BANDS IN TURN
      DO 200 I=1,4
      GO TO (61,62,63,64),I
   61 WRITE(6,102)
  102 FORMAT(1H1, 40X, ' ANTHRACENE HOLE SURFACE BAND IN AC PLANE (10-4
     1EV.)'/)
      GO TO 65
   62 WRITE(6,103)
  103 FORMAT (1H1, 38X, ' ANTHRACENE ELECTRON SURFACE BAND IN AC PLANE (
     110-4 EV)'/)
      GO TO 65
   63 WRITE(6,104)
  104 FORMAT(1H1, 40X, 'NAPHTHALENE HOLE SURFACE BAND IN AC PLANE (10-4
     1EV)'/)
      GO TO 65
   64 WRITE(6,105)
  105 FORMAT (1H1, 38X, 'NAPHTHALENE ELECTRON SURFACE BAND IN AC PLANE (
     110-4 EV)'/)
CALCULATE THE ENERGY IN THREE DIFFERENT DIRECTIONS, K PARALLEL TO
A-1, B-1, AND C-1, RESPECTIVELY
   65 DO 200 J=1,3
CALCULATE KSI AND THE ENERGY FOR DIFFERENT VALUES OF THE ANGLE X FROM 0 TO PI
      DO 100 K = 1,37
      XK=K-1
      ANG(K) = XK/18.0*PI
      X = ANG(K)
      KK=K
      E1(J,K) = 0.0
      E2(J,K) = 0.0
```

```
      E3(J,K) = 0.0
      E4(J,K) = 0.0
      AK(J) = A(I,J) + A1(I,J)*COS(X)
      BK(J) = B(I,J) + B1(I,J)*COS(X/2.0)
      IF (J .NE. 3) GO TO 12
      BK(J) = B(I,J) + B1(I,J)*COS(X)
   12 DK(J) = D(I,J) + D1(I,J)*COS(X)
      ROOT(J) = BK(J)*BK(J) - AK(J)*C(I)
      IF (ROOT(J)) 9, 20, 20
   20 P1 = (-BK(J) + SQRT(ROOT(J)))/AK(J)
      P2 = (-BK(J) - SQRT(ROOT(J)))/AK(J)
      IF (P1 .GE. 0.0 .AND. P2 .LE. 0.0) II=1
      IF (P2 .GE. 0.0 .AND. P1 .LE. 0.0) II=2
      IF (P1 .GE. 0.0 .AND. P2 .GE. 0.0) II=3
      IF (P1 .LE. 0.0 .AND. P2 .LE. 0.0) II=4
      GO TO (1,2,3,4),II
    1 KS1 = 2.0*ALOG(P1)
      KS2 = 2.0*ALOG(-P2)
      GO TO 5
    2 KS1 = 2.0*ALOG(P2)
      KS2 = 2.0*ALOG(-P1)
      GO TO 5
    3 KS1 = 2.0*ALOG(P1)
      KS3 = 2.0*ALOG(P2)
      GO TO 5
    4 KS2 = 2.0*ALOG(-P1)
      KS4 = 2.0*ALOG(-P2)
      GO TO 6
    5 E1(J,K) = (EXP(KS1)+EXP(-KS1))*AK(J) + 2.0*(EXP(KS1/2.0)+
     1 EXP(-KS1/2.0))*BK(J) + DK(J)
      KSI1(J,K) = KS1
      IF (II .EQ. 3) GO TO 7
    6 E2(J,K) = (EXP(KS2)+EXP(-KS2))*AK(J) - 2.0*(EXP(KS2/2.0)+
     1 EXP(-KS2/2.0))*BK(J) + DK(J)
      KSI2(J,K) = KS2
      IF (II .EQ. 4) GO TO 8
      GO TO 10
    7 E3(J,K) = (EXP(KS3)+EXP(-KS3))*AK(J) + 2.0*(EXP(KS3/2.0)+
     1 EXP(-KS3/2.0))*BK(J) + DK(J)
      KSI2(J,K) = KS3
      GO TO 10
    8 E4(J,K) = (EXP(KS4)+EXP(-KS4))*AK(J) - 2.0*(EXP(KS4/2.0)+
     1 EXP(-KS4/2.0))*BK(J) + DK(J)
      KSI1(J,K) = KS4
      GO TO 10
    9 KSI1(J,K) = -BK(J)/AK(J)
      KSI2(J,K) = SQRT(-ROOT(J))/AK(J)
   10 IF (J .EQ. 2) GO TO 11
  100 CONTINUE
      IF (J .EQ. 1) GO TO 11
      WRITE(6,109)
  109 FORMAT(1H1)
   11 WRITE(6,106) J, J, J, J, (ANG(K), KSI1(J,K), KSI2(J,K), E1(J,K),
     1 E2(J,K), E3(J,K), E4(J,K), K=1,KK)
  106 FORMAT(1H0, 10X, 5HANGLE, 13X, 4HKSI+, 14X, 4HKSI-, 12X, 4HEP+(,
     1I1, 3H,K), 10X, 4HEP-(, I1, 3H,K), 10X, 4HEN-(, I1, 3H,K), 10X,
     2 4HEN+(, I1, 3H,K)//(1H , 1P7E18.5))
  200 CONTINUE
      STOP
      END
```

```
THIS PROGRAM CALCULATES THE ELECTRON AND HOLE SURFACE BANDS OF
ANTHRACENE AND NAPHTHALENE IN THE AB PLANE

      DIMENSION A(4,3), B(4,3), C(4), A1(4,3), B1(4,3), ANG(37)
     1, AK(3), BK(3), E1(3,37), E2(3,37), E3(3,37), E4(3,37),
     2 KSI1(3,37), KSI2(3,37), D(4,3), D1(4,3), DK(3), E9(4), E14(4)
      REAL KS1, KS2, KS3, KS4, KSI1, KSI2
READ IN THE VALUES OF THE RESONANCE INTEGRALS FOR VARIOUS GROUPS OF MOLECULES
      READ(5,101) (C(I), I=1,4), ((A(I,J), A1(I,J), I=1,4), J=1,3),
     1 ((B(I,J), B1(I,J), I=1,4), J=1,3), ((D(I,J),D1(I,J),I=1,4),J=1,3)
     2,(E9(I), E14(I), I=1,4)
  101 FORMAT (4F7.2/(8F7.2))
PRINT OUT INPUT DATA
      WRITE(6,107)
  107 FORMAT(1H1,33X,'ANTHRACENE',19X,'NAPHTHALENE'/31X,'HOLE',5X,
     1'ELECTRON',12X,'HOLE',5X,'ELECTRON')
      WRITE(6,108)((A(I,J),I=1,4),(A1(I,J),I=1,4),(B(I,J),I=1,4),
     1 (B1(I,J),I=1,4),J=1,3), C,((D(I,J),I=1,4),(D1(I,J),I=1,4),J=1,3)
     2,(E9(I),I=1,4),(E14(I),I=1,4)
  108 FORMAT('0A(A)=E2+E6+E12+2(E4+E8+E13)',1X,2(F7.2,5X),2(5X,F7.2)/
     1' A1(A)',23X,2(F7.2,5X),2(5X,F7.2)/' B(A)=2(E10+E11)',13X,2(F7.2,
     25X),2(5X,F7.2)/' B1(A)',23X,2(F7.2,5X),2(5X,F7.2)//' A(B)=E2+E6+E1
     32',14X,2(F7.2,5X),2(5X,F7.2)/' A1(B)=2(E4+E8+E13)',10X,2(F7.2,5X),
     42(5X,F7.2)/' B(B)',24X,2(F7.2,5X),2(5X,F7.2)/' B1(B)=2(E10+E11)',
     512X,2(F7.2,5X),2(5X,F7.2)//' A(C)=E2+E6+E12+2(E4+E8+E13)',1X,2(F7.
     62,5X),2(5X,F7.2)/' A1(C)',23X,2(F7.2,5X),2(5X,F7.2)/' B(C)=2(E10+E
     711)',13X,2(F7.2,5X),2(5X,F7.2)/' B1(C)',23X,2(F7.2,5X),2(5X,F7.2)/
     8/' C=ALPHA-ALPHA''',14X,2(F7.2,5X),2(5X,F7.2)//' D(A)=2(E3+E5+2E7)
     9',11X,2(F7.2,5X),2(5X,F7.2)/' D1(A)',23X,2(F7.2,5X),2(5X,F7.2)//
     1' D(B)=2E5',20X,2(F7.2,5X),2(5X,F7.2)/' D1(B)=2(E3+2E7)',13X,2(F7.
     22,5X),2(5X,F7.2)//' D(C)=2(E3+E5+2E7)',11X,2(F7.2,5X),2(5X,F7.2)/
     3' D1(C)',23X,2(F7.2,5X),2(5X,F7.2)//' E9',26X,2(F7.2,5X),2(5X,F7.2
     4)/' E14',25X,2(F7.2,5X),2(5X,F7.2)/)
      PI = 3.141593
CALCULATE THE ENERGY OF EACH OF THE FOUR DIFFERENT BANDS IN TURN
      DO 200 I=1,4
      FE9 = 4.0*E9(I)
      FE14 = 4.0*E14(I)
      GO TO (61,62,63,64),I
   61 WRITE(6,102)
  102 FORMAT(1H1, 40X, ' ANTHRACENE HOLE SURFACE BAND IN AB PLANE (10-4
     1EV)'/)
      GO TO 65
   62 WRITE(6,103)
  103 FORMAT (1H1, 38X, ' ANTHRACENE ELECTRON SURFACE BAND IN AB PLANE (
     110-4 EV)'/)
      GO TO 65
   63 WRITE(6,104)
  104 FORMAT(1H1, 40X, 'NAPHTHALENE HOLE SURFACE BAND IN AB PLANE (10-4
     1EV)'/)
      GO TO 65
   64 WRITE(6,105)
  105 FORMAT (1H1, 38X, 'NAPHTHALENE ELECTRON SURFACE BAND IN AB PLANE (
     110-4 EV)'/)
CALCULATE THE ENERGY IN THREE DIFFERENT DIRECTIONS, K PARALLEL TO
A-1, B-1, AND C-1, RESPECTIVELY
   65 DO 200 J=1,3
CALCULATE KSI AND THE ENERGY FOR DIFFERENT VALUES OF THE ANGLE X FROM 0 TO PI
      DO 100 K = 1,37
      KK=K-1
```

```
      ANG(K) = XK/18.0*PI
      X = ANG(K)
      KK=K
      E1(J,K) = 0.0
      E2(J,K) = 0.0
      E3(J,K) = 0.0
      E4(J,K) = 0.0
      AK(J) = A(I,J) + A1(I,J)*COS(X)
      BK(J) = B(I,J) + B1(I,J)*COS(X/2.0)
   12 DK(J) = D(I,J) + D1(I,J)*COS(X)
      P1 = -C(I)/(AK(J)+BK(J))
      P2 = -C(I)/(AK(J)-BK(J))
      IF (P1 .GE. 0.0 .AND. P2 .LE. 0.0) II=1
      IF (P2 .GE. 0.0 .AND. P1 .LE. 0.0) II=2
      IF (P1 .GE. 0.0 .AND. P2 .GE. 0.0) II=3
      IF (P1 .LE. 0.0 .AND. P2 .LE. 0.0) II=4
      GO TO (1,2,3,4),II
    1 KS1 = ALOG(P1)
      KS2 = ALOG(-P2)
      GO TO 5
    2 KS3 = ALOG(-P1)
      KS4 = ALOG(P2)
      GO TO 7
    3 KS1 = ALOG(P1)
      KS4 = ALOG(P2)
      GO TO 5
    4 KS3 = ALOG(-P1)
      KS2 = ALOG(-P2)
      GO TO 6
    5 E1(J,K) = (EXP(KS1)+EXP(-KS1))*AK(J) + 2.0*(EXP(KS1/2.0)+
     1 EXP(-KS1/2.0))*BK(J) + DK(J) + FE9*COS(X/2.) + FE14*COS(3.0*X/2.)
      KSI1(J,K) = KS1
      IF (II .EQ. 3) GO TO 8
    6 E2(J,K) =-(EXP(KS2)+EXP(-KS2))*AK(J) + 2.0*(EXP(KS2/2.0)+
     1 EXP(-KS2/2.0))*BK(J) + DK(J) - FE9*COS(X/2.) - FE14*COS(3.0*X/2.)
      KSI2(J,K) = KS2
      IF (II .EQ. 1) GO TO 10
    7 E3(J,K) =-(EXP(KS3)+EXP(-KS3))*AK(J) - 2.0*(EXP(KS3/2.0)+
     1 EXP(-KS3/2.0))*BK(J) + DK(J) + FE9*COS(X/2.) + FE14*COS(3.0*X/2.)
      KSI1(J,K) = KS3
      IF (II .EQ. 4) GO TO 10
    8 E4(J,K) = (EXP(KS4)+EXP(-KS4))*AK(J) - 2.0*(EXP(KS4/2.0)+
     1 EXP(-KS4/2.0))*BK(J) + DK(J) - FE9*COS(X/2.) - FE14*COS(3.0*X/2.)
      KSI2(J,K) = KS4
   10 IF (J .NE. 2) GO TO 11
  100 CONTINUE
   11 WRITE(6,106) J, J, J, J, (ANG(K), KSI1(J,K), KSI2(J,K), E1(J,K),
     1 E2(J,K), E3(J,K), E4(J,K), K=1,KK)
  106 FORMAT(1H0, 10X, 5HANGLE, 13X, 4HKSI+, 14X, 4HKSI-, 12X, 4HEP+(,
     1I1, 3H,K), 10X, 4HEP-(, I1, 3H,K), 10X, 4HEN-(, I1, 3H,K), 10X,
     2 4HEN+(, I1, 3H,K)//(1H , 1P7E18.5))
  200 CONTINUE
      STOP
      END
```

```
THIS PROGRAM CALCULATES THE ELECTRON AND HOLE SURFACE BANDS OF
ANTHRACENE AND NAPHTHALENE IN THE BC PLANE
      DIMENSION A(4,3), B(4,3), C(4), A1(4,3), B1(4,3), ANG(37), ROOT(3)
     1, AK(3), BK(3), E1(3,37), E2(3,37), E3(3,37), E4(3,37),
     2 KSI1(3,37), KSI2(3,37), D(4,3), D1(4,3), DK(3), E14(4)
      REAL KS1, KS2, KS3, KS4, KSI1, KSI2
READ IN THE VALUES OF THE RESONANCE INTEGRALS FOR VARIOUS GROUPS OF MOLECULES
      READ(5,101) (C(I), I=1,4), (E14(I), I=1,4),((A(I,J), A1(I,J),
     1I=1,4), J=1,3), ((B(I,J), B1(I,J), I=1,4), J=1,3), ((D(I,J),
     2D1(I,J), I=1,4), J=1,3)
101 FORMAT (4F7.2/4F7.2/(8F7.2))
PRINT OUT INPUT DATA
      WRITE(6,107)
107 FORMAT(1H1,33X,'ANTHRACENE',19X,'NAPHTHALENE'/31X,'HOLE',5X,
     1'ELECTRON',12X,'HOLE',5X,'ELECTRON')
      WRITE(6,108)((A(I,J),I=1,4),(A1(I,J),I=1,4),(B(I,J),I=1,4),
     1 (B1(I,J),I=1,4),J=1,3), C,((D(I,J),I=1,4),(D1(I,J),I=1,4),J=1,3)
     2,(E14(I),I=1,4)
108 FORMAT('0A(A)=E5+E6+E12+2(E7+E8+E13)',1X,2(F7.2,5X),2(5X,F7.2)/
     1' A1(A)',23X,2(F7.2,5X),2(5X,F7.2)/' B(A)=E9+E10+E11+E14',9X,2(F7.
     22,5X),2(5X,F7.2)/' B1(A)',23X,2(F7.2,5X),2(5X,F7.2)//' A(B)=E5+E6+
     3E12',14X,2(F7.2,5X),2(5X,F7.2)/' A1(B)=2(E7+E8+E13)',10X,2(F7.2,5X
     4),2(5X,F7.2)/' B(B)',24X,2(F7.2,5X),2(5X,F7.2)/' B1(B)=E9+E10+E11'
     5,12X,2(F7.2,5X),2(5X,F7.2)//' A(C)=E5+2E7',17X,2(F7.2,5X),2(5X,
     6F7.2)/' A1(C)=E6+2E8+E12+2E13',7X,2(F7.2,5X),2(5X,F7.2)/' B(C)=E9+
     7E14',17X,2(F7.2,5X),2(5X,F7.2)/' B1(C)=E10+E11',15X,2(F7.2,5X),
     82(5X,F7.2)//' C=ALPHA-ALPHA''',14X,2(F7.2,5X),2(5X,F7.2)//' D(A)=2
     9(E2+E3+2E4)', 11X,2(F7.2,5X),2(5X,F7.2)/' D1(A)',23X,2(F7.2,5X),
     12(5X,F7.2)//' D(B)=2E2',20X,2(F7.2,5X),2(5X,F7.2)/' D1(B)=E3+2E4',
     216X,2(F7.2,5X),2(5X,F7.2)//' D(C)=2E3',20X,2(F7.2,5X),2(5X,F7.2)/
     3' D1(C)=E2+2E4',16X,2(F7.2,5X),2(5X,F7.2)//' E14',25X,2(F7.2,5X),
     42(5X,F7.2)/)
      PI = 3.141593
CALCULATE THE ENERGY OF EACH OF THE FOUR DIFFERENT BANDS IN TURN
      DO 200 I=1,4
      GO TO (61,62,63,64),I
 61 WRITE(6,102)
102 FORMAT(1H1, 40X, ' ANTHRACENE HOLE SURFACE BAND IN BC PLANE (10-4
     1EV)'/)
      GO TO 65
 62 WRITE(6,103)
103 FORMAT (1H1, 38X, ' ANTHRACENE ELECTRON SURFACE BAND IN BC PLANE (
     110-4 EV)'/)
      GO TO 65
 63 WRITE(6,104)
104 FORMAT(1H1, 40X, 'NAPHTHALENE HOLE SURFACE BAND IN BC PLANE (10-4
     1EV)'/)
      GO TO 65
 64 WRITE(6,105)
105 FORMAT (1H1, 38X, 'NAPHTHALENE ELECTRON SURFACE BAND IN BC PLANE (
     110-4 EV)'/)
CALCULATE THE ENERGY IN THREE DIFFERENT DIRECTIONS, K PARALLEL TO
A-1, B-1, AND C-1, RESPECTIVELY
 65 DO 200 J=1,3
CALCULATE KSI AND THE ENERGY FOR DIFFERENT VALUES OF THE ANGLE X FROM 0 TO PI
      DO 100 K = 1,37
      XK=K-1
      ANG(K) = XK/18.0*PI
      X = ANG(K)
```

```
      KK=K
      E1(J,K) = 0.0
      E2(J,K) = 0.0
      E3(J,K) = 0.0
      E4(J,K) = 0.0
      AK(J) = A(I,J) + A1(I,J)*COS(X)
      BK(J) = B(I,J) + B1(I,J)*COS(X)
      IF (J .NE. 2) GO TO 12
      BK(J) = B(I,J) + B1(I,J)*COS(X/2.0) + E14(I)*COS(3.0*X/2.0)
   12 DK(J) = D(I,J) + D1(I,J)*COS(X)
      ROOT(J) = BK(J)*BK(J) - AK(J)*C(I)
      IF (ROOT(J)) 9, 20, 20
   20 P1 = (-BK(J) + SQRT(ROOT(J)))/AK(J)
      P2 = (-BK(J) - SQRT(ROOT(J)))/AK(J)
      IF (P1 .GE. 0.0 .AND. P2 .LE. 0.0) II=1
      IF (P2 .GE. 0.0 .AND. P1 .LE. 0.0) II=2
      IF (P1 .GE. 0.0 .AND. P2 .GE. 0.0) II=3
      IF (P1 .LE. 0.0 .AND. P2 .LE. 0.0) II=4
      GO TO (1,2,3,4),II
    1 KS1 = 2.0*ALOG(P1)
      KS2 = 2.0*ALOG(-P2)
      GO TO 5
    2 KS1 = 2.0*ALOG(P2)
      KS2 = 2.0*ALOG(-P1)
      GO TO 5
    3 KS1 = 2.0*ALOG(P1)
      KS3 = 2.0*ALOG(P2)
      GO TO 5
    4 KS2 = 2.0*ALOG(-P1)
      KS4 = 2.0*ALOG(-P2)
      GO TO 6
    5 E1(J,K) = (EXP(KS1)+EXP(-KS1))*AK(J) + 2.0*(EXP(KS1/2.0)+
     1 EXP(-KS1/2.0))*BK(J) + DK(J)
      KSI1(J,K) = KS1
      IF (II .EQ. 3) GO TO 7
    6 E2(J,K) = (EXP(KS2)+EXP(-KS2))*AK(J) - 2.0*(EXP(KS2/2.0)+
     1 EXP(-KS2/2.0))*BK(J) + DK(J)
      KSI2(J,K) = KS2
      IF (II .EQ. 4) GO TO 8
      GO TO 10
    7 E3(J,K) = (EXP(KS3)+EXP(-KS3))*AK(J) + 2.0*(EXP(KS3/2.0)+
     1 EXP(-KS3/2.0))*BK(J) + DK(J)
      KSI2(J,K) = KS3
      GO TO 10
    8 E4(J,K) = (EXP(KS4)+EXP(-KS4))*AK(J) - 2.0*(EXP(KS4/2.0)+
     1 EXP(-KS4/2.0))*BK(J) + DK(J)
      KSI1(J,K) = KS4
      GO TO 10
    9 KSI1(J,K) = -BK(J)/AK(J)
      KSI2(J,K) = SQRT(-ROOT(J))/AK(J)
   10 IF (J .EQ. 1) GO TO 11
  100 CONTINUE
      IF (J .EQ. 2) GO TO 11
      WRITE(6,109)
  109 FORMAT(1H1)
   11 WRITE(6,106) J, J, J, J, (ANG(K), KSI1(J,K), KSI2(J,K), E1(J,K),
     1 E2(J,K), E3(J,K), E4(J,K), K=1,KK)
  106 FORMAT(1H0, 10X, 5HANGLE, 13X, 4HKSI+, 14X, 4HKSI-, 12X, 4HEP+(,
     1I1, 3H,K), 10X, 4HEP-(, I1, 3H,K), 10X, 4HEN-(, I1, 3H,K), 10X,
     2 4HEN+(, I1, 3H,K)//(1H , 1P7E18.5))
  200 CONTINUE
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          THIS PROGRAM NUMERICALLY EVALUATES THE MOBILITY TENSOR IN
          THE RELAXATION TIME APPROXIMATION.  THE INTEGRAL IS
          EVALUATED OVER 13X13 POINTS USING THE TRAPEZOIDAL RULE FOR
          THE ELECTRON AC SURFACE BAND OF NAPHTHALENE.
      COMMON E(14,1), A, B, C, D
      DIMENSION DEP(3), DEN(3), S1(   9,13), SA11(   9,13), S22(   4),
     1SA12(   9,13), SA13(   9,13), SA22(   9,13), SA23(   9,13),
     2SA33(   9,13), S2(   9), SB(   9,3), ST(3), S12(   4,25),
     3SAB11(   4,25), SAB12(   4,25), SAB13(   4,25), SAB22(   4,25),
     4SAB23(   4,25), SAB33(   4,25), SBB(   4,3), SCB(3), SC(3)
      READ(5,101) E
101   FORMAT (7F7.2)
      WRITE(6,99)
 99   FORMAT(1H1, 7X,9HHOLE BAND,7X,13HELECTRON BAND//)
      DO 701 I2=2,14
701   WRITE(6,102) I2, E(I2,1)
102   FORMAT(1H , I2, 17X, F17.2)
EXPRESS BETA(=1/KT), AT 300 DEG. K, IN UNITS OF 10-4 EV.
      BETA=-1.0/(1.38054E-16*300.0*6.24196E15)
EXPRESS PLANCK'S CONSTANT IN UNITS OF 10-4 EV-SEC.
      H=(1.05450E-27*6.24196E15)
      H2=H*H
      PI=3.141593
      A=8.235
      B=6.003
      C1=8.658
      ANG=2.145301
      C=C1*SIN(ANG)
      D=C1*COS(ANG)
      FX=(C1-A*COS(ANG)-2.0*D*COS(ANG))/(A*C*SIN(ANG))
      VXI=(A*A+C1*C1+2.0*A*D)*PI/(A*C*C)
      VXK=(A*A+C1*C1+2.0*A*D)*PI/(A*A*C+A*C*D)
      VAI=PI/(A*SIN(ANG)*SIN(ANG))
      VAK=PI/(A*SIN(ANG)*COS(ANG))
      I=1
      DO 300 K=1,9
      X=(K-1)*PI*FX/12.0
      DO 200 L=1,13
      Z=(L-1)*PI/(12.0*C)
      A1=X*D+Z*C
      A3=X*A
      CALL  INT(I,A1,A3,EP,EN,DEP,DEN)
BEGIN CALCULATION OF INTEGRALS
      S1(   K,L)=EXP(BETA*EP)+EXP(BETA*EN)
      SA11(   K,L)=DEP(1)*DEP(1)*EXP(BETA*EP)+DEN(1)*DEN(1)*EXP(BETA*EN)
      SA13(   K,L)=DEP(1)*DEP(3)*EXP(BETA*EP)+DEN(1)*DEN(3)*EXP(BETA*EN)
200   SA33(   K,L)=DEP(3)*DEP(3)*EXP(BETA*EP)+DEN(3)*DEN(3)*EXP(BETA*EN)
      S2(   K)=(S1(   K,1)+S1(   K,13))*PI/(12.0*C)
      SB(   K,1)=(SA11(   K,1)+SA11(   K,13))*PI/(12.0*C)
      SB(   K,2)=(SA13(   K,1)+SA13(   K,13))*PI/(12.0*C)
      SB(   K,3)=(SA33(   K,1)+SA33(   K,13))*PI/(12.0*C)
      DO 300 L=2,12
      S2(   K)=S2(   K)+S1(   K,L)*PI/(6.0*C)
      SB(   K,1)=SB(   K,1)+SA11(   K,L)*PI/(6.0*C)
      SB(   K,2)=SB(   K,2)+SA13(   K,L)*PI/(6.0*C)
300   SB(   K,3)=SB(   K,3)+SA33(   K,L)*PI/(6.0*C)
      S3=S2(1)/2.0
      DO 401 M=1,3
```

```
  401 SC(M)=SB(1,M)/2.0
      DO 402 K=2,9
      S3=S3+S2(K)
      DO 402 M=1,3
  402 SC(  M)=SC(  M)+SB(  K,M)
      DO 310 K=1,4
      X=(K+8)*PI*FX/12.0
      ZL=(X/VXI-1.0)*VXK
      ZU=(X/VAI-1.0)*VAK
      DO 210 L=1,25
      Z=(L-13)*PI/(12.0*C)
      ZP=(L-12)*PI/(12.0*C)
      ZM=(L-14)*PI/(12.0*C)
      IF (ZL.GT.Z.AND.ZL.LT.ZP) GO TO 10
      IF (ZU.LT.Z.AND.ZU.GT.ZM) GO TO 20
      IF (Z.LT.ZL.OR.Z.GT.ZU) GO TO 210
      GO TO 3
   10 Z=ZL
      LL=L+1
      L1=L
      GO TO 3
   20 Z=ZU
      LU=L-1
      L2=L
    3 A1=X*D+Z*C
      A3=X*A
      CALL INT(I,A1,A3,EP,EN,DEP,DEN)
      S12(  K,L)=EXP(BETA*EP)+EXP(BETA*EN)
      SAB11(  K,L)=DEP(1)*DEP(1)*EXP(BETA*EP)+DEN(1)*DEN(1)*EXP(BETA*EN)
      SAB13(  K,L)=DEP(1)*DEP(3)*EXP(BETA*EP)+DEN(1)*DEN(3)*EXP(BETA*EN)
      SAB33(  K,L)=DEP(3)*DEP(3)*EXP(BETA*EP)+DEN(3)*DEN(3)*EXP(BETA*EN)
  210 CONTINUE
      S22(  K)=((S12(  K,L1)+S12(  K,LL))*((LL-13)*PI/(12.0*C)-ZL)+
     1(S12(  K,L2)+S12(  K,LU))*(ZU-(LU-13)*PI/(12.0*C))-S12(  K,LL)*PI/
     2(12.0*C)-S12(  K,LU)*PI/(12.0*C))/2.0
      SBB(  K,1)=((SAB11(  K,L1)+SAB11(  K,LL))*((LL-13)*PI/(12.0*C)-ZL)
     1+(SAB11(  K,L2)+SAB11(  K,LU))*(ZU-(LU-13)*PI/(12.0*C))-
     2(SAB11(  K,LL)+SAB11(  K,LU))*PI/(12.0*C))/2.0
      SBB(  K,2)=((SAB13(  K,L1)+SAB13(  K,LL))*((LL-13)*PI/(12.0*C)-ZL)
     1+(SAB13(  K,L2)+SAB13(  K,LU))*(ZU-(LU-13)*PI/(12.0*C))-
     2(SAB13(  K,LL)+SAB13(  K,LU))*PI/(12.0*C))/2.0
      SBB(  K,3)=((SAB33(  K,L1)+SAB33(  K,LL))*((LL-13)*PI/(12.0*C)-ZL)
     1+(SAB33(  K,L2)+SAB33(  K,LU))*(ZU-(LU-13)*PI/(12.0*C))-
     2(SAB33(  K,LL)+SAB33(  K,LU))*PI/(12.0*C))/2.0
      DO 310 L=LL,LU
      S22(  K)=S22(  K)+S12(  K,L)*PI/(12.0*C)
      SBB(  K,1)=SBB(  K,1)+SAB11(  K,L)*PI/(12.0*C)
      SBB(  K,2)=SBB(  K,2)+SAB13(  K,L)*PI/(12.0*C)
  310 SBB(  K,3)=SBB(  K,3)+SAB33(  K,L)*PI/(12.0*C)
      S32=S22(4)/2.0
      DO 403 M=1,3
  403 SCB(  M)=SBB(  4,M)/2.0
      DO 404 K=1,3
      S32=S32+S22(K)
      DO 404 M=1,3
  404 SCB(  M)=SCB(  M)+SBB(  K,M)
      S3=S3+S32
      DO 400 M=1,3
  400 SC(  M)=SC(  M)+SCB(  M)
      DO 500 M=1,3
  500 ST(M)=SC(M)/(S3*H2)*1.0E-16
```

```
      WRITE(6,104)
  104 FORMAT(1H0,52X,13HELECTRON BAND//1H0,5X,11HDENOMINATOR,49X,
     18HMOBILITY/1H ,29X,5HV(AA),11X,5HV(AC),11X,5HV(CC)/)
      WRITE(6,105) S3, ST
  105 FORMAT(1H0, 1PE16.4, 5X, 3E16.4)
      STOP
      END
      SUBROUTINE INT(I,A1,A3,EP,EN,DEP,DEN)
THIS SUBROUTINE CALCULATES THE VALUES OF E+ AND E-, AND OF DE+/DK, AND DE-/DK,
FOR EACH POINT IN THE INTEGRAL.
      COMMON E(14,1), A, B, C, D
      DIMENSION DEPM(3),DEP(3),DEN(3),DEMP(3)
      A4=A1+A3
      A5=A3/2.0
      A7=A1+A5
      A8=A1-A5
      A9=A1-A3
      U=E(3,I)+2.0*(E(4,I)*COS(A1)+E(7,I)*COS(A3)+E(8,I)*COS(A4)+E(13,I)
     1*COS(A9))
      V=E(9,I)*COS(A5)+E(10,I)*COS(A7)+E(11,I)*COS(A8)
      W=-146.11
      ROOT=V*V-U*W
      IF (ROOT .LT. 0.0) STOP
      P1=(-V+SQRT(ROOT))/U
      P2=(-V-SQRT(ROOT))/U
      IF (P1 .GE. 0.0 .AND. P2 .LE. 0.0) II=1
      IF (P2 .GE. 0.0 .AND. P1 .LE. 0.0) II=2
      IF (P1 .GE. 0.0 .AND. P2 .GE. 0.0) II=3
      IF (P1 .LE. 0.0 .AND. P2 .LE. 0.0) II=3
      GO TO (1,2,3), II
    1 AP=2.0*ALOG(P1)
      AN=2.0*ALOG(-P2)
      GO TO 4
    2 AP=2.0*ALOG(P2)
      AN=2.0*ALOG(-P1)
      GO TO 4
    3 STOP
    4 A6=AP/2.0
      A2=AN/2.0
      EPM=2.0*(E(9,I)*COS(A5)         +E(10,I)*COS(A7)          +E(11,I)*
     1COS(A8))*(EXP(A6)+EXP(-A6))
      EMP=2.0*(E(9,I)*COS(A5)         +E(10,I)*COS(A7)          +E(11,I)*
     1COS(A8))*(EXP(A2)+EXP(-A2))
      E1= E(3,I)+2.*(E(4,I)*COS(A1)+E(7,I)*COS(A3)+E(8,I)*COS(A4)+
     1E(13,I)*COS(A9))
      EP=2.0*(E(2,I)*COS(A1)+E(5,I)*COS(A3)+E(6,I)*COS(A4)+E(12,I)*
     1COS(A9))+E1*(EXP(AP)+EXP(-AP))+EPM
      EN=2.0*(E(2,I)*COS(A1)+E(5,I)*COS(A3)+E(6,I)*COS(A4)+E(12,I)*
     1COS(A9))+E1*(EXP(AN)+EXP(-AN))-EMP
CALCULATE DERIVATIVES, DE/DK
      DEPM(1)=-    (E(9,I)*A*SIN(A5)          +2.*E(10,I)*(D+.5*A)*SIN(A7)
     1         +2.*E(11,I)*(D-.5*A)*SIN(A8))*(EXP(A6)+EXP(-A5))
      DEMP(1)=-    (E(9,I)*A*SIN(A5)          +2.*E(10,I)*(D+.5*A)*SIN(A7)
     1         +2.*E(11,I)*(D-.5*A)*SIN(A8))*(EXP(A2)+EXP(-A2))
      D1=(E(4,I)*D*SIN(A1)+E(7,I)*A*SIN(A3)+E(8,I)*(D+A)*SIN(A4)+
     1E(13,I)*(D-A)*SIN(A9))
      DEP(1)=-2.0*(E(2,I)*D*SIN(A1)+E(5,I)*A*SIN(A3)+E(6,I)*(D+A)*
```

```
     1SIN(A4)+E(12,I)*(D-A)*SIN(A9)+D1*(EXP(AP)+EXP(-AP)))+DEPM(1)
      DEN(1)=-2.0*(E(2,I)*D*SIN(A1)+E(5,I)*A*SIN(A3)+E(6,I)*(D+A)*
     1SIN(A4)+E(12,I)*(D-A)*SIN(A9)+D1*(EXP(AN)+EXP(-AN)))-DEMP(1)
      DEPM(3)=-2.0*C*(E(10,I)*SIN(A7)           +E(11,I)*SIN(A8))*
     1(EXP(A6)+EXP(-A6))
      DEMP(3)=-2.0*C*(E(10,I)*SIN(A7)           +E(11,I)*SIN(A8))*
     1(EXP(A2)+EXP(-A2))
      D3=E(4,I)*SIN(A1)+E(8,I)*SIN(A4)+E(13,I)*SIN(A9)
      DEP(3)=-2.*C*(E(2,I)*SIN(A1)+E(6,I)*SIN(A4)+E(12,I)*SIN(A9)+D3*
     1(EXP(AP)+EXP(-AP)))+DEPM(3)
      DEN(3)=-2.*C*(E(2,I)*SIN(A1)+E(6,I)*SIN(A4)+E(12,I)*SIN(A9)+D3*
     1(EXP(AN)+EXP(-AN)))-DEMP(3)
      RETURN
      END
```

THIS PROGRAM NUMERICALLY EVALUATES THE MOBILITY TENSOR IN THE RELAXATION TIME APPROXIMATION. THE INTEGRAL IS EVALUATED OVER 13 POINTS USING THE TRAPEZOIDAL RULE FOR THE HOLE BC SURFACE BAND OF NAPHTHALENE.

```
      COMMON A, B, C, D, E(14)
      DIMENSION DEP(3), DEN(3), X(2), S1(13), S22(13)
      READ(5,101) E
  101 FORMAT(7F7.2)
      WRITE(6,99)
   99 FORMAT(1H1, 7X,9HHOLE BAND,7X,13HELECTRON BAND//)
      DO 701 I2=2,14
  701 WRITE(6,102) I2, E(I2)
  102 FORMAT(1H , I2,  F17.2)
      BETA= 1.0/(1.38054E-16*300.0*6.24196E15)
      H=(1.05450E-27*6.24196E15)
      H2=H*H
      PI=3.141593
      A=8.235
      B=6.003
      C1=8.658
      ANG=2.145301
      C=C1*SIN(ANG)
      D=C1*COS(ANG)
      X(1)=0.0
      X(2)=PI
      DO 200 L=1,2
      DO 300 K=1,13
      Y=(K-1)*PI/(12.0*B)
      A1=X(L)
      A2=Y*B
      CALL INT( A1,A2,EP,EN,DEP,DEN)
      S1(K)=EXP(BETA*EP)+EXP(BETA*EN)
  300 S22(K)=DEP(2)*DEP(2)*EXP(BETA*EP)+DEN(2)*DEN(2)*EXP(BETA*EN)
      S2=(S1(1)+S1(13))/2.0
      SB   =(S22(1)+S22(13))/2.0
      DO 301 K=2,12
      S2 = S2 + S1(K)
  301 SB   =SB    +S22(K)
      ST   =SB    /(S2*H2)*1.0E-15
      WRITE(6,103)
  103 FORMAT(1H0,10X,9HHOLE BAND,10X,8HMOBILITY//1H ,5X,11HDENOMINATOR,
     113X,5HV(B3)//)
```

```
      WRITE(6,105) S2, ST
105   FORMAT(1H0, 1PE16.4, 5X,  E16.4)
200   CONTINUE
      STOP
      END

      SUBROUTINE INT(A1,A2,EP,EN,DEP,DEN)
      COMMON A, B, C, D, E(14)
      DIMENSION DPM(3), DMP(3), DEP(3), DEN(3)
      A3=A2/2.0
      A4=3.0*A3
      U=E(5)+(E(6)+E(12))*COS(A1)+2.*(E(7)+(E(8)+E(13))*COS(A1))*COS(A2)
      V=(E(9)+(E(10)+E(11))*COS(A1))*COS(A3)+E(14)*COS(A4)
      W=-149.98
      ROOT=V*V-U*W
      IF (ROOT .LT. 0.0) STOP
      P1=(-V+SQRT(ROOT))/U
      P2=(-V-SQRT(ROOT))/U
      IF (P1 .GE. 0.0 .AND. P2 .LE. 0.0) II=1
      IF (P2 .GE. 0.0 .AND. P1 .LE. 0.0) II=2
      IF (P1 .GE. 0.0 .AND. P2 .GE. 0.0) II=3
      IF (P1 .LE. 0.0 .AND. P2 .LE. 0.0) II=4
      GO TO (1,2,3,4), II
    1 AP=2.0*ALOG(P1)
      AN=2.0*ALOG(-P2)
      GO TO 5
    2 AP=2.0*ALOG(P2)
      AN=2.0*ALOG(-P1)
      GO TO 5
    3 AP=2.0*ALOG(P1)
      AN=2.0*ALOG(P2)
      GO TO 5
    4 STOP
    5 A5=AP/2.0
      A6=AN/2.0
      E1=2.0*(E(9)*COS(A3)+(E(10)+E(11))*COS(A1)*COS(A3)+E(14)*COS(A4))
      EPM=E1*(EXP(A5)+EXP(-A5))
      EMP=E1*(EXP(A6)+EXP(-A6))
      F2=E(5)+(E(6)+E(12))*COS(A1)+(E(7)+(E(8)+E(13))*COS(A1))*COS(A2)
     1*2.0
      EP=2.0*(E(2)*COS(A1)+E(3)*COS(A2))+4.0*E(4)*COS(A1)*COS(A2)+E2*
     1(EXP(AP)+EXP(-AP))+EPM
      EN=2.0*(E(2)*COS(A1)+E(3)*COS(A2))+4.0*E(4)*COS(A1)*COS(A2)+E2*
     1(EXP(AN)+EXP(-AN))-EMP
      IF (II .EQ. 3) EN=EN+2.0*EMP
      D2=B*SIN(A3)*(E(9)+(E(10)+E(11))*COS(A1))+3.0*B*E(14)*SIN(A4)
      DPM(2)=-D2*(EXP(A5)+EXP(-A5))
      DMP(2)=-D2*(EXP(A6)+EXP(-A6))
      DE2=-2.0*B*(E(7)+(E(8)+E(13))*COS(A1))*SIN(A2)
      DEP(2)=-B*(2.0*E(3)+4.0*E(4)*COS(A1))*SIN(A2)+DE2*(EXP(AP)+
     1EXP(-AP))+DPM(2)
      DEN(2)=-B*(2.0*E(3)+4.0*E(4)*COS(A1))*SIN(A2)+DE2*(EXP(AN)+
     1EXP(-AN))-DMP(2)
      IF (II .EQ. 3) DEN(2)=DEN(2)+2.0*DMP(2)
      RETURN
      END
```

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