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A MOLECULAR ORBITAL TREATMENT OF CHEMICAL REACTIVITY

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INTRODUCTION

This thesis treats the addition of reagents to butadiene by simple LCAO–MO (linear combination of atomic orbitals–molecular orbital) theory. The purpose is to determine if, neglecting overlap and configuration interaction, qualitative predictions of reactivity can be made correctly. In particular, the treatment is concerned with the positively charged transition state assumed to exist during butadiene addition reactions.

Reactions for which one may assume an activated complex are particularly interesting, since the closer the structure defined in formulating the calculations approximates the actual transition state, the more realistic will be the conclusions obtained. Thus for a relatively simple starting point the choice has been to study more or less in detail the reaction between 1,3-butadiene and electrophilic reagents such as the hydrogen halides or in some cases the halogens themselves. Even in this case many simplifications are required. The suggested reaction is believed[1] to progress through two steps; first the electrophilic attack of the proton on the end carbon atom, then a second step involving nucleophilic attack by the halogen ion or a halogen-containing complex.

The question of why the proton adds preferentially to the end carbon atom has already been approached[2] in terms of charge densities and other criteria for reactivity. The details of this treatment will be used in introducing this treatment of the activated complex. There remains, then, the investigation of the intermediate ion in order to find what specific quantum-mechanical properties one may associate with the successful prediction of the position of predominant addition of the halide ion.

Following this initial inquiry, the information obtained therein has been used to make further studies on the second step of the reaction, the halide nucleophilic attack on the intermediate involving butadiene, as well as to make brief investigations of isoprene and chloroprene. The latter work has been done applying both single and SCF (self-consistent field) calculations. The iterative results are less amenable to critical analysis, but they are desirable and interesting from the point of view of the interrelation of certain quantum chemical parameters when approximating relative reactivities of various positions in reacting species.

The reactivity parameters used to establish theoretically the position of electrophilic or nucleophilic attack, include atom stabilization energies and frontier electron charge densities.

In the case of addition of hydrogen halides to butadiene and the related molecules considered hyperconjugation or second order conjugation is accounted for. In this way the proper resonance and inductive effects for the experimentally established 1,2-addition are produced in the assumed transition state complex.

Finally a brief discussion is included of the methods used in carrying out the rather lengthy calculations, accomplished by means of an I.B.M. 704 electronic computer. This discussion is incorporated in the appendix.

HISTORY AND BACKGROUND

EARLY DEVELOPMENTS

> It is the behaviour and distribution of the electrons around the nucleus that give the fundamental character of an atom; it must be the same for molecules. In one sense, therefore, the description of the bonds in any molecule is simply the description of the electron distribution in it.[3]

We seek, consequently, a way of describing, in the broad sense, the distribution of electrons in the reacting species. We are acquainted with the Bohr treatment of the atom and the discrete energy states containing electrons making their way in specified paths around the nucleus. We are also familiar with later developments by Schroedinger, Heisenberg and others which describe the wavelike character and probability of electrons existing in any given space and time.

As the atom was being studied in further detail, approaches to the understanding of the binding forces in molecules were made. First the hydrogen molecule-ion, then hydrogen, then heteronuclear systems such as HF and others were investigated. With each step toward polyatomic systems, however, came the necessity for greater and greater approximations, leading away from the rigorous mathematical treatments deemed desirable for greatest accuracy. Furthermore, the best results were and still are accompanied in large measure by the use of empirical data such as spectra and ionization energies.

The use of this experimentally determined evidence has been of considerable value, nevertheless, in the quantum theory of electronic structure in molecules, and together with the valence bond method developed by Heitler and London, the later-appearing molecular orbital method of Hückel, Hund and Mulliken, and Lennard-Jones have made significant strides in giving us a deeper insight into valence forces, electronic spectra, and chemical reactivity.

QUANTUM CHEMISTRY AND REACTIVITY

Molecular orbital theory in its early stages of development was used on the problem of the detailed electronic structure of diatomic molecules. Work by Hund, Mulliken, and Lennard-Jones[4] treated each electron as having a quantized angular momentum about the molecular axis. When one considers a sigma electron, the momentum is zero, while a pi electron has a value of the momentum of 1. This is analagous to the s,p,d,f notation in atoms, including the Pauli exclusion principle.

These concepts were particularly valuable in interpreting molecular spectra in terms of electronic transitions between molecular energy states. The molecule was considered to be intermediate between two separate atoms and a united form containing all the electrons of both individual atoms.

As an outgrowth of this type of interpolation came the "Aufbau" Principle which assigns the electrons one by one to a molecule, and places them in the lowest available molecular and atomic levels.

Theoretical studies on molecular structure at this time were being approached by two separate and seemingly widely divergent methods, namely through the presently discussed molecular orbital theory, and also through the valence bond method of Heitler and London. Wheland[5] ventured a comparison of the two methods, regarding especially unsaturated and aromatic organic molecules. He found that while the valence bond method strongly emphasizes the covalent character of bonds, the M.O. approach is less rigorous and does not take proper account of the Pauli exclusion principle, with the result that there is an extreme piling up of electrical charges in the molecule and an over emphasis of its ionic character. Nevertheless, the latter method is mathematically simpler and can be applied to a wider variety of problems, such as the energy relations among hydrocarbons, the dissociation of aryl substituted ethanes, etc.

Moreover, though agreement is still not complete, one can allow for configuaration interaction in the molecular orbital approach and allow for a greater number of ionic structures in the valence bond approach to reach a more consistent and probably more accurate picture of the true electronic structure of molecules. Configuration interaction accounts for a certain amount of influence of one M.O. on another, whereas in the simplified approach each M.O. is linearly dependent only on the atomic orbitals of one energy state. This interaction is determined by the form of the Hamiltonian operator (not LCAO) used in evaluating the energy of the system. The Hamiltonian form of the wave equation will be discussed in the next section. The present work takes no account of the interaction of electron configurations..

In dealing with the Hund, Mulliken, and Hückel method of treating unsaturated and aromatic molecules, the first direct attempts at determining chemical reactivity were made by Wheland and Pauling[6] and later by Wheland[7]. The main emphasis was on determining the orientation of substituents in aromatic molecules. These workers took into account two factors, first the permanent charge distribution in the aromatic molecule, and also the changes in this permanent charge distribution caused by the approaching group in a chemical reaction.

This charge distribution is affected by the inductive effect and also by the resonance effect. Since we are dealing with electrophilic substitution in this case, the greater the electronic charge density, the greater the relative rate of substitution of the approaching group for hydrogen on the particular carbon atom involved. The charge distribution in an aromatic or otherwise unsaturated molecule is affected through the inductive effect by the electronegativity of any substituent on this molecule, whereas the charge distribution as affected by the resonance effect can be accounted for through the valence bond method, considering the more stable resonance structures, each of which makes a certain contribution, and will illustrate in one way or another the charge distribution throughout the molecule.

Wheland and Pauling[6] used the perturbation treatment to show the effect of electronegativity differences on the permanent polarization of the molecule through the inductive effect. This is done by changing the electronegativity of a given atom by altering the value of the coulombic integral, a parameter to be discussed in more detail later.

As regards the polarizability of the molecule-its susceptibility to change of electronic charge density upon the approach of a charged reagent-only small corrections are usually involved; however, in some cases it is of decisive importance. At times it is the permanent polarization which determines the chemical reactivity of a given position, whereas in other circumstances it is the polarizability of the electrons in this position which predominates in determining permanent polarization with a certain amount of attention to crude estimates of polarizability.

A further development brought about by Wheland[7] considers not charge, but the energies of the structures contributing to the activated complex. Thus with energy calculations we have a means for determining the susceptibility of a position to electrophilic, nucleophilic, or radical attack. Later treatments of charge densities also allow this much latitude in predictivity when <u>frontier</u>

orbitals are considered.

Still more investigations were carried out by Coulson[8] who also summarized several approaches of other authors quite lucidly. In this paper he discusses, among other factors, charge distribution, free valence, and partial bond orders. These will be discussed in greater detail in the next section.

A detailed analysis has been made of the electronic behavior in conjugated molecules, both hydrocarbons and hetero-systems, by Coulson and Longuet-Higgins.[9,10,11,12] In a series of papers they define and treat analytically such quantities as mutual atom polarizability, mutual bond polarizability, atom self-polarizability, and show their importance in determining the effect of structural changes on chemical reactivity. They also discuss the relation of these quantities to other chemical properties.

By using a first order perturbation treatment these workers were able to evaluate the relationship between the several polarizabilities and the coefficients of the atomic orbitals and the orbital energies. They also showed that when one alters slightly the coulomb integral of an alternant hydrocarbon (aromatic hydrocarbon or polyene containing no odd-membered unsaturated rings), the electron densities are alternately increased and decreased throughout the molecule, thus providing a theoretical basis for the empirical law of alternating polarity in conjugated systems containing a hetero-atom. Pyridine would exemplify this behavior.

An application of hyperconjugation as a means to more accurately describing hydrocarbon electronic structures was suggested by Mulliken and his co-workers.[13] They recognized that the $C{\equiv}H_3$ group should have the power to conjugate with other groups containing double or triple bonds, and the name hyperconjugation, or second order conjugation, was proposed for this effect. For example, the difference between the conjugating power of the $C{\equiv}CH$ group and the $C{\equiv}H_3$ group is mainly quantitative and not qualitative, so that the molecular orbital calculations can be based on changes of the parameters related to the strength of the bond involved. Though the triple bond in the $C{\equiv}CH$ group is much more saturated than the triple bond in the $C{\equiv}H_3$ group, there is less (but still appreciable) tendency to conjugate than the latter.

Mulliken gives a strong argument in favor of the hyperconjugative phenomenon by comparing the calculated and empirical conjugation energies using the heats of combustion of C-H and C-C bonds.

A series of papers by Dewar[14] appeared in 1952 indicating the importance of the transition state theory of reactivity in molecular orbital calculations. He compared the three ways of attack in chemical reactivity, namely, the reactivity which is determined by differential charge densities at various positions in the reactant molecule, reactivity determined by free valence, and reactivity determined by the energy differences between initial and transition states of various reacting species.

In this series of papers Dewar set forth 73 basic theorems devoted to the prediction of reactivity. He emphasizes that when charge densities show nothing concerning the susceptibility of attack of various positions, that is, when the charge densities of all atoms are identical as is sometimes the case with alternant hydrocarbons, polarizabilities take over as a means for predicting reactivity.

He further points out that the validity of the methods used in the electrostatic theory, including charge densities and free valences, depend upon correlation with the energy required to remove one atom in an even alternant hydrocarbon from conjugation, and that the latter is the primary factor in determining the position at which a reaction will take place in a molecule.

Another work of interest is a book by Pullman and Pullman.[15] Among other physicochemical factors such as dipole moments and spectra these authors discuss many of the results obtainable through M.O. theory of reactivity and use molecular diagrams to illustrate these results as Coulson[3] has also done. Both substitution reactions and addition reactions are covered and attention is given to dynamic as well as static factors.

R. D. Brown[16] established still more meaning for M. O. calculations in terms of a simplified version of the theory of absolute reaction rates. He compared this localization also referred to by Dewar[14] with some of the other methods of approximating reactivity such as charge density, bond order, and free valence, the quantities defined in the isolated molecule approximation.

In defining the kinetic basis of the theoretical treatment, Brown depicts a series of curves showing the rise and fall of the pi electron energy throughout a given reaction. It is interesting to note that a crossing of the energy curves of two positions in the molecule as shown in figure 1 indicates that kinetic control of reactivity predominates over thermodynamic control. Thus atom r is more susceptible to attack than atom s, but under proper conditions rearrangement might take place to form a molecule with an effective result of attack on atom s. This is in fact the case in certain additions to dienes to form allylic products as we shall discuss later. This requires careful attention to the experimental results chosen for comparison with theory.

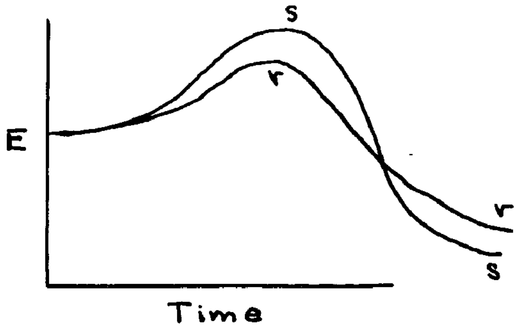

Figure 1

π Electron Energy

Until 1952 the concept of electron charge density at any atom carried with it the inference that it is the <u>total</u> pi electron density at this point which determines chemical reactivity, and that we must in such a case refer only to electrophilic reactivity. Furthermore, when one considered even alternant hydrocarbons such as butadiene, with a total charge density of unity at each atom, the electrostatic approach had to be discarded and recourse was made to polarizabilities as criteria for reactiveness. This necessity, of course, has no reasonable justifications. At this time Fukui and co-workers[17] conceived the idea of using not the total electron density, but the frontier electron density as a criterion for judging relative chemical reactivity among a number of positions in a molecule.

For electrophilic reactivity the frontier electrons would be those occupying the highest occupied orbital, whereas for nucleophilic attack on an atom the frontier orbital would be the lowest unoccupied orbital. Hence these would serve as more accurate determining factors for estimating attracting power for charged reagents. Their justification lay partly in the assumption that the highest occupied orbital is attractive to an electrophilic attacking reagent in the formation of the transition complex, and that lower-lying orbitals are repulsive.

Though Greenwood[18] has been critical of certain applications of this approach, we believe that knowledge of the frontier electron distribution in a molecule or transition state complex can be a valuable means for estimating positions of preferential attack by either nucleophilic or electrophilic reagents.

In a still more recent contribution Nakajima[19] has defined another quantity for determing reactivity, namely, atom stabilization energy, which is based (in electrophilic substitution) on the removal of almost one pi electron from the reactant toward the reagent. Use of this and another parameter, the atom energy, will be illustrated in more detail later.

The most recent contributions to the molecular orbital theory of organic reactions are papers published by Pilar.[20] A new method is applied to the transition state complex wherein addition to butadiene of a positive ion results in an intermediate considered to contain a pseudo-heteroatom consisting of the attacking reagent, the end carbon atom which it attacks, and the next adjacent carbon atom. The complex is then depicted as a three atom system with two occupied orbitals and one unoccupied orbital.

The treatment is general in that it emphasizes the trend required in relative values of resonance and coulombic integrals for proper prediction of the experimental results of normal addition reactions of an ionic nature. Pilar points out the usefulness of frontier electron densities and atom stabilization energies in his treatment of the activated complex.

This approach seems to be a particularly valuable one in that it emphasizes group interaction rather than explicitly accounting for each atom in the system.

THEORY AND METHODS

In this section we shall discuss first the fundamentals of the molecular orbital theory including the use of the wave equation and the variation principle, several of the criteria for chemical reactivity, and a detailed treatment of butadiene as a means to introducing our present method of approaching an estimation of chemical reactivity. A more detailed discussion can be obtained by referring to any of the standard texts dealing with quantum chemistry.[21,22,23]

THE WAVE EQUATION AND THE VARIATION PRINCIPLE

Unsaturated molecules can be considered to contain three kinds of electrons, inner shell electrons not associated with bond formation, outer shell electrons forming sigma bonds of axial symmetry, and finally pi electrons, which are considerably less localized than sigma electrons and are located in antisymmetric p orbitals. Without considering interactions with nuclei or other kinds of electrons, concern is limited only to the latter mobile pi electrons. They may therefore be assigned unique wave functions, say for the molecule as a whole in which conjugation is involved.

Expressing the wave equation in terms of this so-called eigenfunction we have

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 \Psi_{(x)}}{\partial x^2} + V_{(x)}\Psi_{(x)} = E\Psi_{(x)} \qquad (1)$$

h = Planck's constant

m = mass of electron

$\Psi_{(x)}$ = total molecular wave function referred to x-axis

V(x) = potential energy

E = total pi electron energy

The left hand side of this equation may now be defined as operating on $\Psi_{(x)}$, this operation being called H, the Hamiltonian operator with motion in one direction and excluding time. More generally,

$$H\Psi = E\Psi \qquad (2)$$

But Ψ, the total molecular wave function for all electrons, can be expressed as a product of 1-electron molecular wave functions ψ as follows in a system of n atoms

$$\Psi = \prod_{n} \psi_j \qquad (3)$$

from which, returning to the operator form of the wave equation, one obtains

$$H\psi_j = E_j\psi_j \qquad (4)$$

for each one-electron molecular orbital.

The molecular orbital wave functions, ψ_j*, are taken to be linear combinations of the atomic wave functions, ϕ_{rj} .

$$\psi_j = \sum_{r=1}^{n} C_{rj} \phi_r \qquad (5)$$

Notice that there will be n atomic orbitals which form n molecular orbitals differing from each other in the signs and magnitudes of the coefficients C_{rj}. Moreover, one could also form an atom Hamiltonian

$$H \phi_r = \epsilon \phi_r \qquad (6)$$

At this point let us pause and compare the relative simplicity of this approach with one which utilizes many-electron wave functions. If one considers a polyatomic molecule to contain several pi electrons, then each electron may interact with the other at some time during the existence of the molecule. The number of combinations in such an exchange phenomenon increases exponentially with the size of the molecule and with the number of electrons. The result can be an extremely complicated mathematical treatment. Such is the nature of valence bond theory, though it is true one retains a simple picture of the molecule in its various

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*Subscripts j, k will be used to signify energy levels, while r, s, t, will denote atoms referred to.

resonance structures, each defined by a weighted molecular wave function.

It is interesting to observe that the two theories approach each other in correctly defining the true electronic state of the molecule, as one counteracts the excessive consideration of electron exchange (covalency) in the valence bond method by including in the calculations more ionic resonance forms, and as one accounts for the interaction of the electrons in different molecular orbitals (configurations) in the M.O. approach. (Also see page 6.)

It is now reasonable to elaborate on M.O. theory by discussing the application of the variation method as a means of approximating the form of the wave functions. The only truly exact wave mechanical solution to date is that for the hydrogen molecule-ion, a very simple system indeed compared to butadiene.

In M.O. theory one doesn't need the complete wave function so we shall concern ourselves with ψ_j and ϕ_r . The precise form of the latter need not be known, but as a matter of convenience it is considered to be the 2pz wave function for atom r, antisymmetric and perpendicular to the xy plane containing the sigma bonds.

To start, one chooses trial functions of ψ in order to find the lowest possible value of E, that closest to the true energy. This is done by minimizing with respect to the a.o. coefficients, since the distinguishing assumption has been made that the one-electron molecular orbital is a linear combination of all the atomic orbitals involved in conjugation (resonance).

$$H\psi = E\psi \tag{7}$$

$$\psi^* H\psi = \psi^* E\psi \tag{8}$$

Where ψ^* is the complex conjugate of ψ and is included only in calculations of magnetic properties and the like, from which one obtains, integrating over all space, and assuming ψ to be real,

$$E = \frac{\int \psi H \psi \, d\tau}{\int \psi^2 \, d\tau} \tag{9}$$

Minimizing,

$$\frac{\partial E}{\partial C_r} = 0 \quad (r = 1, 2, \text{----} n) \tag{10}$$

hence

$$C_r (H_{rr} - E) + \Sigma' C_s (H_{rs} - ES_{rs}) = 0 \tag{11}$$

where H_{rs} is the matrix component of H in the system ϕ_r, and is defined by

$$H_{rs} = \int \phi_r H \phi_s \, d\tau = \beta_{rs}$$ =resonance integral for r≠s (12)

$$= \alpha_r$$ = coulombic integral for r=s

$$S_{rs} = \int \phi_r \phi_s \, d\tau =$$ overlap integral for r≠s (13)

There is one equation of type (11) for each of the n values of s and the ' after the summation sign indicates that the term with r=s is omitted from the sum. Neglecting overlap so that $S_{rs}=0$ for r≠s, since complete orthogonality of atomic wave functions is assumed we suppose that the a.o.'s are individually normalized, requiring that $S_{rr}=1$. Normalization in this case is the condition that the total probability that the electron associated with ϕ_r exists within the limits of the space defined by τ is unity, or $\int \phi^2 d\tau = 1$. In other words, the square of a wave function is a measure of the probability density of the electron associated with it.

One can now write

$$C_r(H_{rr} - E) + C_s \sum_r{}' H_{rs} = 0 \qquad r = 1, 2, --- n \tag{14}$$

or if it is implicitly understood that all of the foregoing approximations and assumptions are applied,

$$\sum c(H - ES) = 0 \tag{15}$$

which are known as the secular equations. If the β's and C's are real, then the following is also true

$$\Sigma\,(H-ES) = 0 = \mathrm{Det}\,(H-ES) \tag{16}$$

which in expanded secular determinant form can be shown as

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} & \text{———} & \text{———} \\ \beta_{21} & \alpha_2 - E & \beta_{23} & \text{———} & \text{———} \\ \beta_{31} & \text{———} & \text{———} & \text{———} & \text{———} \\ \text{———} & \text{———} & \text{———} & \text{———} & \text{———} \\ \text{———} & \text{———} & \text{———} & \text{———} & \alpha_n - E \end{vmatrix} = 0 \tag{17}$$

From the n roots (see appendix) of this equation one may find the ratios of the a.o. coefficients by substitutions in the original secular equations and if one considers the normalization conditions

$$\sum_{r=1}^{n} C_{rj}^{2} = 1 \tag{18}$$

the absolute magnitudes are fixed. (also see appendix)

CRITERIA FOR CHEMICAL REACTIVITY

Having determined the solutions of this secular determinant (eigenvalues) and the a.o. coefficients (eigenvectors) one can now evaluate from these quantities several parameters useful in estimating chemical reactivity.

Total pi electron charge density. The total density of pi electrons in the vicinity of atom r is

$$Q_r = 2 \sum_{j=1}^{m} C_{rj}^2 \qquad (19)$$

where m is the highest occupied orbital

Total mobile bond order. Mobile (excluding sigma bonds) bond order is defined as

$$P_{rs} = 2 \sum_{j=1}^{m} C_{rj} C_{sj} \qquad (20)$$

between atoms r and s. The factor of 2 in the above two formulas expresses the limitation of the Pauli exclusion principle, there being possible a maximum of 2 electrons per orbital. (In the case of free radicals there is but one electron in the highest occupied orbital.) One use of bond orders is in predicting bond lengths.

Free valence. This factor includes sigma and pi bonds such that

$$F_r = 3 + \sqrt{3} - N_r \qquad (21)$$

where N_r = mobile bond order=number of sigma bonds attached to atom r. This measures susceptibility to radical attack.

Frontier electron charge density.

$$Q_{rf} = 2 C_{rf}^2 \qquad (22)$$

where the frontier level is defined as the highest occupied level in electrophilic attack on atom r, or the lowest unoccupied level in nucleophilic attack, the pi electrons being assigned to the lowest levels, two per orbital.

Atom energy.

$$E_r = 2 \sum_{j=1}^{m} C_{rj}^2 \qquad (23)$$

It can be seen that the total pi electron energy is given by

$$E = \sum_{r=1}^{n} E_r \qquad (24)$$

Atom stabilization energy.

$$\mathcal{E}_r^+ = E_r - C_{rf}^2 \qquad (25)$$

for electrophilic attack, and

$$\mathcal{E}_r^- = E_r + C_{rf}^2 \qquad (26)$$

for nucleophilic attack, recalling the proper definition of frontier level in each case. Atom stabilization energy is a measure of the energy needed to promote the pi electrons of an atom to the valence state (E_j=0).

Atom self-polarizability.

$$\Pi_{rr} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{C_{rj}^{2} \cdot C_{rk}^{2}}{\epsilon_{j} - \epsilon_{k}} \qquad (27)$$

This parameter determines the ease of displacement of pi electrons upon the approach of a charged reagent.

Other reactivity factors. Other reactivity parameters include atom-bond polarizabilities[9], atom localization energies[16], etc., but these will not be considered.

DETAILED TREATMENT OF BUTADIENE

Taking the one-electron molecular orbital ψ one determines the energy as

$$E = \frac{\int \psi H \psi \, d\tau}{\int \psi^{2} \, d\tau} \qquad (28)$$

and using the LCAO approximation, including neglect of non-neighbor interactions such that all integrals refer to adjacent atoms, one arrives at the following expressions for ψ and E.

$$E = \frac{C_1^2H_{11} + C_2^2H_{22} + C_3^2H_{33} + C_4^2H_{44}}{C_1^2 + C_2^2 + C_3^2 + C_4^2 + C_1C_2S_{12} + C_2C_3S_{23} + C_3C_4S_{34}} \qquad (30)$$

$$+ \frac{2(C_1C_2H_{12} + C_2C_3H_{23} + C_4C_4H_{34})}{C_1^2 + C_2^2 + C_3^2 + C_4^2 + C_1C_2S_{12} + C_2C_3S_{23} + C_3C_4S_{34}} = \frac{N}{D}$$

N and D are defined for convenience in the following step.

Next E is minimized with respect to each coefficient, thereby yielding the secular equations.

$$\frac{\partial E}{\partial C_1} = \frac{D(2C_1H_{11} + 2C_2H_{12}) - N(2C_1S_{11} + 2C_2S_{12})}{D^2} = 0 \qquad (31)$$

Doing the same for C_2, C_3, and C_4, one gets

$$C_1(H_{11}-ES_{11}) + C_2(H_{12}-ES_{12}) = 0 \qquad (32)$$

$$C_1(H_{12}-ES_{12}) + C_2(H_{22}-ES_{22}) + C_3(H_{23}-ES_{23}) = 0 \qquad (33)$$

$$C_2(H_{23}-ES_{23}) + C_3(H_{33}-ES_{33}) + C_4(H_{34}-ES_{34}) = 0 \qquad (34)$$

$$C_3(H_{34}-ES_{34}) + C_4(H_{44}-ES_{44}) = 0 \qquad (35)$$

In this approximation overlap is neglected, hence all $S_{rs}=0$ for $r \neq s$ and the a.o.'s are assumed to be separately normalized, so $S_{rr}=1$. Furthermore, the substitutions for α and β are made before forming the secular determinant. Note, meanwhile, the approximate physical significance of these integrals. The coulombic integrals, α_r, depend upon the electron density near atom r, and hence are related in some degree to electronegativity, while the resonance integrals, β_{rs}, can be assumed to be related to the strength of the r-s bond.[9] From equation (16) one forms the secular determinant, noting that (36)

$$\begin{vmatrix} (\alpha_1-E) & \beta_{12} & 0 & 0 \\ \beta_{12} & (\alpha_2-E) & \beta_{23} & 0 \\ 0 & \beta_{23} & (\alpha_2-E) & \beta_{34} \\ 0 & 0 & \beta_{34} & (\alpha_4-E) \end{vmatrix} = 0 \qquad (37)$$

In these calculations there is no particular significance attached to the absolute value of β_{rs}. Thus all quantities in the secular equation are expressed in units of some β, say β_o. Mathematically this involves dividing the entire equation by β_o. For this calculation we will make the additional assumptions that all resonance integrals are equal to β_o, and that all coulombic integrals are equal and zero. The latter are to be used as the zero reference from which all energies will be measured. The secular determinant now takes the simple form

$$\begin{vmatrix} -E & 1 & 0 & 0 \\ 1 & -E & 1 & 0 \\ 0 & 1 & -E & 1 \\ 0 & 0 & 1 & -E \end{vmatrix} = 0 \qquad (38)$$

with roots of 1.6180, 0.6180, -0.6180, and -1.6180. Since resonance integrals are negative quantities these eigenvalues are in increasing order of magnitude, the two lowest being the occupied orbitals. One could construct an energy diagram

E_4---------------------- -1.6180

E_3---------------------- -0.6180

---------------------- 0.0000

E_2---------------------- 0.6180

E_1---------------------- 1.6180

Having obtained the eigenvalues, one determines the a.o. coefficients (normalized eigenvectors). From the secular equations (32-35) one first finds the ratios of coefficients in terms of C_1.

$$C_2 = C_1E \tag{39}$$

$$C_3 = C_1(E^2-1) \tag{40}$$

$$C_4 = C_1(E^3-2E) \tag{41}$$

To obtain the value of C_1 we use the normalization condition

$$C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1 \tag{42}$$

$$C_1^2(1 + E^2 + (E^2-1)^2+(E^3-2E)^2) = 1 \tag{43}$$

from which one may obtain all the a.o. coefficients for each value of E. It should be pointed out, however, that should our β values differ from unity, these would also appear in the equation defining the ratios of the a.o. coefficients.

Knowing the eigenvalues and eigenvectors it is a simple matter to calculate values of the quantities we shall be concerned with in the remainder of this thesis, namely, charge densities, bond orders, atom energies, and atom stabilization energies according to the methods outlined on pages 20 and 21. One may first express the occupied molecular orbitals as

$$\psi_2 = .6015\,\phi_1 + .3720\,\phi_2 + .3720\,\phi_3 + .6015\,\phi_4 \qquad (44)$$

$$\psi_1 = .3720\,\phi_1 + .6015\,\phi_2 + .6015\,\phi_3 + .3720\,\phi_4 \qquad (45)$$

The remaining results are summarized in Table 1.

Table 1

Butadiene Parameters

	1	2	3	4
H_{rr}	0	0	0	0
H_{rs}	1.0	1.0	1.0	
Q_{rf}	.725	.175	.175	.725
Q_r	1.0	1.0	1.0	1.0
P_{rs}	.8944	.4476	.8944	
ε_r	.8944	1.2416	1.3416	.8944
ε_r^+	.6708	1.2526	1.1526	.6708

The next step is to consider the activated complex which will undergo nucleophilic attack. This problem will be dealt with in the next section using the methods outlined here. The importance of taking into account explicitly the differences in resonance integrals is emphasized in Pilar's work[20]. He assumes the following skeletal structure for the intermediate.

$$\left[R-C-C-C-C\right]^{+}$$

Two of the four pi electrons have been removed from conjugation, and the R which has attached itself to the terminal carbon atom, together with this carbon and its neighbor, can be considered to make up a pseudo heteroatom contributing one "atomic" orbital to what is now a three "atom" system. This intermediate ion can thus be expressed as

$$Q_2 \overset{K\beta}{\text{———}} C_3 \overset{\beta}{\text{———}} C_4$$

The k that Pilar defines as a proportionality constant between resonance integrals indicates the nature of the ratio between β_{23} and β_{34}. It turns out from his calculations that when k is unity, β_{23} and β_{34} are equal, and the resultant charge densities and atom stabilization energies are identical on "atom" 2 and atom 4, making it impossible to indicate which course the reaction will take in the nucleophilic stage. When the k is greater or less than unity, however, as in the case when R is more or less electronegative than carbon, respectively, the predomination of addition can be readily predicted from the reactivity parameters to be on the #2 atom in the former case and on the #4 atom in the latter. Hence the need for adjustment of beta values.

Though table 1 gives values of the reactivity parameters qualitatively in keeping with experimental results, one knows that the approximation of all resonance integrals being equal to unity does not truly represent the state of the butadiene molecule. Since we know that there is more pi bonding between carbon atoms 1 and 2 than between 2 and 3, we might well reduce β_{23} and perhaps raise β_{12} a little and see how much change this brings about in the relative values of the reactivity parameters. Though this variety of perturbation treatment is useful and will be applied to the activated complex, an even more realistic improvement on this initial calculation can be made in the way of a self-consistent determination of reaction parameters.

In order to decide upon what basis for self-consistency to use, consider the connection between β and bond order, which we might assume to be linear. As has already been stated, relationships between bond order and bond distance have been obtained. Coulson[2] illustrates this graphically. Actually the correlation here used is based initially on the variation of overlap integral with bond distance.

From Mulliken's[24] values of bond distances vs. overlap integrals based on Slater atomic orbitals we first assume that for the small changes in bond distance dealt with here, there is approximately a linear relationship. This is far from true for the entire range of values reported by Mulliken, but the bond distances in question are of the order of 1.33-1.54 Angstroms, so the approximation will not be a great deal out of the way. Also, as will be demonstrated later in the case of the protonated butadiene activated complex, the self-consistent results are not very sensitive to small variations in the iterative constants.

Furthermore, it is known that resonance integrals are roughly proportional to overlap integrals. One may derive, therefore, assuming the β_{12} to be unity, the approximate linear relationship

$$\beta_{rs} = .387\ P_{rs} + .653 \qquad (46)$$

and, using this, calculate new resonance integrals for each bond, repeating the computations of eigenvalues and eigenvectors. From the normalized a.o. coefficients again bond orders and new resonance integrals can be obtained, the iterative process being repeated until the new β and those just previously calculated agree satisfactorily. The results with 4 iterations for butadiene, the consecutive resonance integrals agreeing within 0.002, are given in table 2.

$$\psi_2 = .5843\,\phi_1 + .3983\,\phi_2 - .3983\,\phi_3 - .5843\,\phi_4 \qquad (47)$$

$$\psi_1 = .3983\,\phi_1 + .5843\,\phi_2 + .5843\,\phi_3 + .3983\,\phi_4 \qquad (48)$$

Table 2

Iterative Butadiene Parameters

Atom or Bond Number

	1	2	3	4
E_1-E_4	1.4859	.6903	-.6903	-1.4859
H_{rr}	0	0	0	0
H_{rs}	1.0128	.7956	1.0128	
Q_{rf}	.6828	.3172	.3172	.6828
Q_r	1.0	1.0	1.0	1.0
P_{rs}	.9308	.3656	.9308	
e_r	.9427	1.2335	1.2335	.9427
e_r^+	.7070	1.1240	1.1240	.7070

RESULTS AND DISCUSSION

EXAMPLES OF FIRST AND SECOND ORDER CONJUGATION

The previous section dealt with the theory and methods in the MO calculations used for this thesis. At this point a discussion is in order of the results obtained from the use of these methods of determining the chemical reactivity of several molecules and their activated complexes in hydrohalogenation.

The first concern will be to treat a single molecule by the method elaborated on in the previous section with one important ramification. Hyperconjugation, or no-bond resonance, is a phenomenon easily treated by MO theory and the method first used by Mulliken for accounting for this so-called second order conjugation will be used. The first molecule to be thus treated will be propylene and it will be depicted as

$$\begin{array}{ccccccc} H_3 & \equiv & C & - & CH & = & CH_2 \\ 1 & & 2 & & 3 & & 4 \end{array}$$

where position 1 indicates the existence of a pseudo heteroatom containing 3 hydrogens. The triple bond associated with "atoms" 1 and 2 is thus assumed to have a certain degree of conjugating ability with the C_3-C_4 pi bond.

The justification for the p orbital character of atoms 1 and 2 is illustrated by Coulson[8] who assigns the positions of the H atoms such that it is conceivable to construct such an orbital, slightly distorted, but at right angles to the sigma bond of atoms 2 and 3 and which satisfies certain symmetry requirements.

For calculating purposes the next problem is to assign realistic values for the coulombic and resonance integrals, which one does according to Coulson and Crawford.[25] The H_3 pseudo-atom is assumed to have an electronegativity less than that of carbon, a supposition which shows up in the value taken for the coulombic integral. Since one is dealing with α values in terms of β_o , the basic value must be changed such that the diagonal element

$$H_{11} = \alpha + \delta_1 \beta \tag{49}$$

where δ_1 is the parameter adjusting H_3 to the correct electronegativity.

The greater the electronegativity the smaller (less positive) is H_{11}, therefore, δ_1 , to show a smaller electron attracting power than carbon (α =0), must be a negative value, since β_o is negative. It turns out in the calculation of the dipole moment of toluene that both α_1 and α_2 (coulombic integrals for "atoms" 1 and 2) require values different from that of carbon, with $\delta_1 = -.5$ and $\delta_2 = -.1$, which will appear in the secular determinant as the respective α values. One shouldn't commit too great an error in adopting these values for a $C \equiv H_3$ group attached to any system, as a first approximation.

The values of β are also taken from the paper by Coulson and Crawford, with β_{12} =2.5 and β_{23} =0.7, in keeping with the concept of a relatively high degree of localization of electrons in the $C\equiv H_3$ "pi" bond.

The secular determinant for propylene, therefore, will have the same form as that for butadiene, with the noted differences in α_r and β_{rs}. In fact, in the symbolic program for the computer evaluation of the matrices and reactivity parameters involved, one need only supply separate sets of input data to the same program for either molecule. (It will be evident later that the same situation prevails for isoprene and protonated chloroprene.) It is also desirable to know the iterative results for propylene. The results of the single computation are shown in table 3, while the self-consistent values are in table 4.

Table 3

Propylene Reactivity Parameters

	Atom or Bond Number			
	1	2	3	4
H_{rr}	−.5	−.1	0	0
H_{rs}	2.5	0.7	1.0	
Q_{rf}	.1148	.0375	.8563	.9913
Q_r	.9143	1.0756	.9938	1.0163
ε_r	1.9845	2.4730	1.1189	.9799
ε_r^+	1.9311	2.4556	.7210	.5192

Table 4

SCF Propylene Reactivity Parameters

Atom or Bond Number

	1	2	3	4
H_{rr}	−.5	−.1	0	0
H_{rs}	1.0014	.8016	1.0096	
Q_{rf}	.6005	.5936	.1565	.6494
Q_r	.7603	1.1661	.9886	1.0850
ε_r	.5206	1.0931	1.2386	.9297
ε_r^+	.2204	.7963	1.1604	.6050

The remainder of this thesis is restricted for the most part to considerations of values of the integrals, frontier electron densities, atom energies, and atom stabilization energies. We note that the singly computed total pi electron charge densities of table 3 are in almost identical agreement with the values of Crawford. Fukui[26] gives values of frontier electron densities which are substantially different from those of table 1; however,

$$Q_{1f} + Q_{2f} < Q_{3f} < Q_{4f} \qquad (50)$$

which is the same as the order of Fukui's values. Moreover, the method by which the latter author arrived at these figures is not defined in his paper. He may or may not have considered hyperconjugation, since the values of the present author's atoms 1 and 2 can be combined to indicate the charge density of the methyl group as may be the case with Fukui's results.

In consideration of the experimental results and interpretation one may refer to Wheland.[1] It is evident from table 3 that the results of this author agree with the experimental factor that the proton (or halogen ion in the case of halogenation) will add initially to the terminal carbon atoms of the double bond. This is a result of

$$Q_{4f} > Q_{3f}, \quad \mathcal{E}_4 < \mathcal{E}_3, \quad \mathcal{E}_4^{+} < \mathcal{E}_3^{+} \qquad (51)$$

One might also add the inequality $Q_4 > Q_3$, but note that $Q_2 > Q_4$, which would suggest the physically improbable addition of the proton to the carbon of the methyl group. Though it is possible that one is justified in ignoring any attack that is not conceivable chemically, it is more satisfying when the theoretical predictions do not have this factor to contend with. Furthermore, it has already been demonstrated in the case of butadiene in the previous section that total charge densities can be misleading as criteria for electrophilic reactivity.

These latter observations are even more in evidence for the results shown in table 4, which exemplifies 5 iterations with a β consistency of 0.002, input β's being identical with those in table 1.

$$Q_{3f} > Q_{4f} \qquad (52)$$

$$Q_4 > Q_3 \qquad (53)$$

$$\mathcal{E}_4 < \mathcal{E}_3 \qquad (54)$$

$$\mathcal{E}_4^+ < \mathcal{E}_3^+ \qquad (55)$$

$$Q_{1f} > Q_{2f} > Q_{3f} \qquad (56)$$

$$Q_2 > Q_3 \qquad (57)$$

$$\mathcal{E}_1 < \mathcal{E}_4 , \quad \mathcal{E}_2 < \mathcal{E}_3 \qquad (58)$$

$$\mathcal{E}_1^+ < \mathcal{E}_4^+ , \quad \mathcal{E}_2^+ < \mathcal{E}_3^+ \qquad (59)$$

It would be tempting to use chemical intuition here in the light of physical improbability and ignore the disagreeable predictions if it were not for the computed resonance integrals that arise from this series of iterations. When one compares those β's for the single computation with the self-consistent results, one finds that

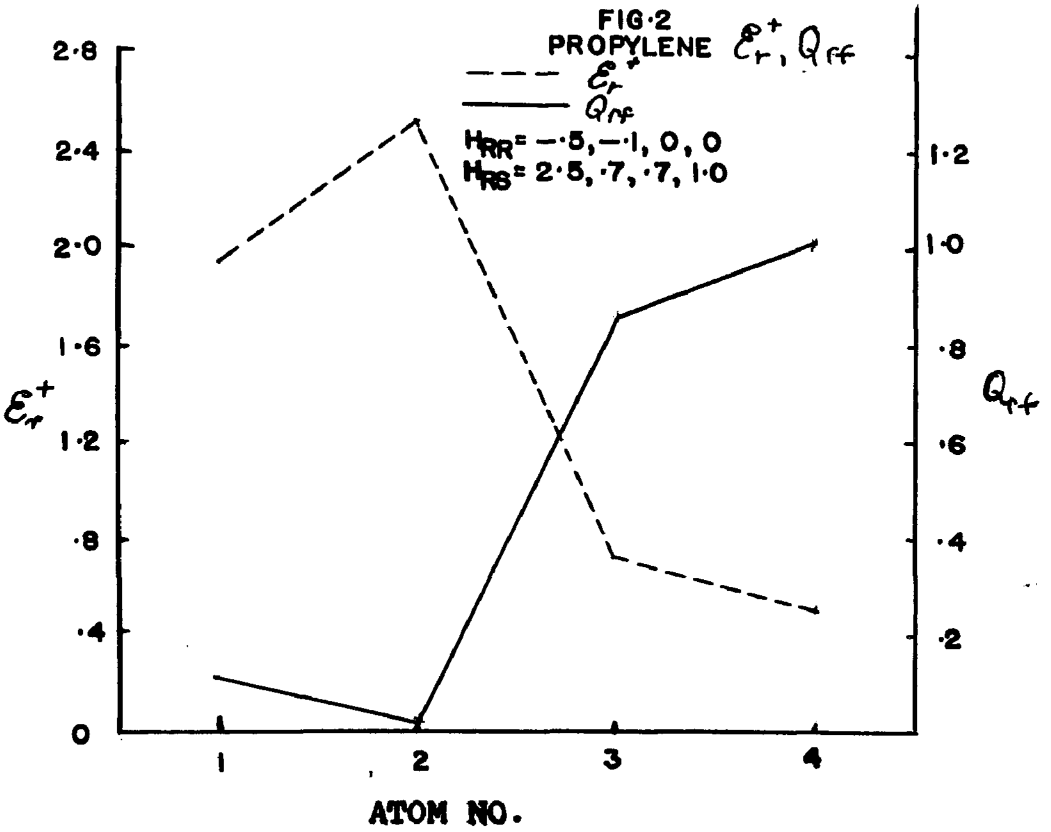
$$\beta_{12} > \beta_{23} < \beta_{34} , \qquad \beta_{12} > \beta_{34} \qquad (60)$$

$$\beta_{12} > \beta_{23} < \beta_{34} , \qquad \beta_{12} < \beta_{34} \qquad (61)$$

respectively. That β_{12} should be even approximately equal to β_{34} violates the admittedly crude concept of the physical significance of the resonance integral. One is almost assured from the nature of the approximations that the localization of the bonding electrons between atoms 1 and 2 is appreciably greater than that between atoms 3 and 4. Therefore, one must conclude that this iterative determination, though it correctly favors electrophilic attack of atom 4 over atom 3, at the same

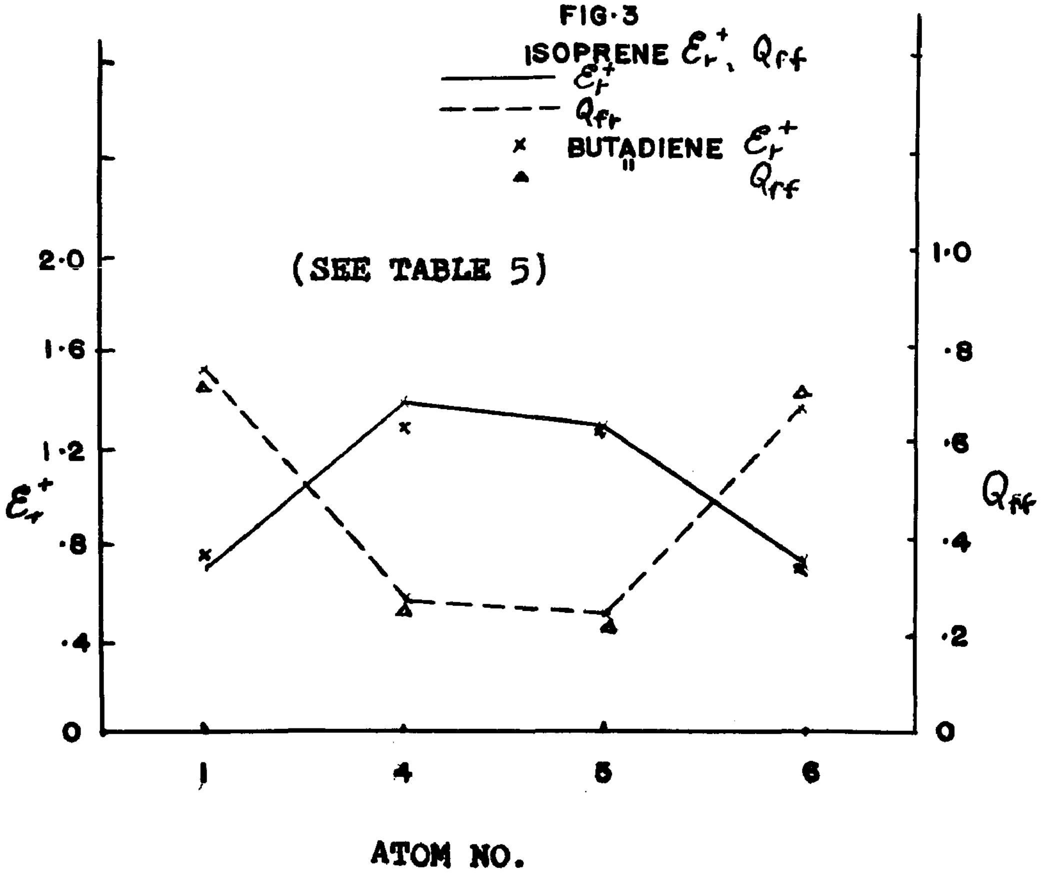
FIG·2

PROPYLENE $\mathcal{E}_r^+, Q_{rf}$



FIG·3

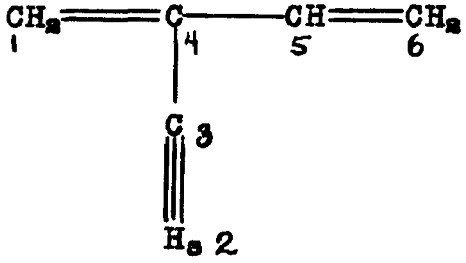
ISOPRENE $\mathcal{E}_r^+, Q_{rf}$



time it decidedly overemphasizes the resonance interaction between the $H_3\equiv C$ group and the $CH=CH_2$ group as a result of an unfavorable "choice" of β's forced upon it by the conditions of iteration.

Without resorting to further iterative determinations involving propylene to correct this defect, the frontier charge densities and atom stabilization energies of tables 3 and 4 are depicted graphically. Figure 2 thus shows the maxima in frontier electron densities and minima in atom stabilization energies as being the positions of most likely attack by electrophilic reagents.

To study a system with a greater degree of conjugation consider isoprene and the results expressed in tables 5 and 6 respectively for the single and iterative computations. Resonance integrals are listed in the order β_{14}, β_{23}, β_{34}, β_{45} β_{56}, with the atom numbers indicated in the accompanying structural formula. The SCF results represent 5 iterations at a self-consistency of 0.002 with initial integrals identical in values with those in table 5.



$$\underset{1}{CH_2}=\underset{4}{C}(-\underset{3}{C}\equiv \underset{2}{H_3})-\underset{5}{CH}=\underset{6}{CH_2}$$

Table 5

Isoprene Reactivity Parameters

Atom or Bond Number

	1	2	3	4	5	6
H_{rr}	0	−.5	−.1	0	0	0
H_{rs}	1.0	2.5	.7	1.0	1.0	
Q_{rf}	.7557	.0282	.0055	.2759	.2500	.6846
Q_f	1.0134	.9152	1.0762	.9956	1.0008	.9987
$\mathcal{E}_r$	.8797	1.9904	2.4692	1.4467	1.3351	.8969
$\mathcal{E}_r^+$	.6514	1.9819	2.4676	1.3633	1.2596	.6901

Table 6

SCF Isoprene Reactivity Parameters

Atom or Bond Number

	1	2	3	4	5	6
H_{rr}	0	−.5	−.1	0	0	0
H_{rs}	.9884	1.0042	.7923	.7851	1.0160	
Q_{rf}	.7407	.4939	.4359	.1626	.0321	.1547
Q_r	1.0795	.7648	1.1679	.9901	1.0010	.9967
$\mathcal{E}_r$	.8566	.5284	1.0802	1.4102	1.2208	.9532
$\mathcal{E}_r^+$	.6851	.4186	.9792	1.3725	1.2133	.9174

There are several interesting observations to be made from this data. First of all one is now dealing with a 6-electron system (3 orbitals), and it is the atomic orbital coefficients of the third orbital which defines the frontier charge density, whereas with butadiene, for example, it was the second orbital in which one was interested in terms of this reactivity parameter. There is a choice of four positions for the proton to attack which are chemically reasonable. One would expect that there would be at least some similarity with butadiene in case of electrophilic attack and that there is more likelihood that this would occur at the end carbons (1 and 6) than at atoms 4 and 5. Also the methyl group should have some effect on the reactivity parameters. Thus atom 1 is favored in the initial attack, as evidenced both by Q_{1f} and $\mathcal{E}_1^+$ in comparison with Q_{6f} and $\mathcal{E}_6^+$, which is verified by experiment.

To carry the analogy with butadiene a step further, notice the small triangles in Fig. 3 indicating the frontier electron charge densities as calculated previously for butadiene. The quantitative comparison is good indeed though we are dealing with ψ_3 in one case and ψ_2 in the other. Even more interesting is the effect the $C{\equiv}H_3$ group has on the frontier electron distribution. The frontier charge residing on the methyl group amounts to about .03, a good indication of the direction of its inductive effect toward the remainder of the molecule, where over 98% of the frontier charge is located. This allows the conveniently direct comparison of these four atoms with the butadiene system. It is apparent that the CH_3 group causes a perturbation, bringing about an increase in the relative frontier charges on atoms 1, 4, and 5 (1,2, and 3 in the butadiene system) at the expense of atom 6. It is suggested that this can be a primary driving force deciding the fate of the approaching reagent, which must favor attack on atom 1.

The question might arise as to whether one should place this much emphasis on what seems to be only a small difference (.76 <u>vs</u>. .68) in electron density or atom stabiliation energy (.65 <u>vs</u>. .69). However, if one considers the very rough approximation

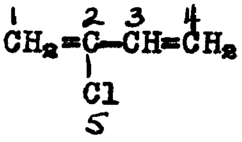
$$P_1/P_6 = \exp\left[\left(\mathcal{E}_6^{\ddagger} - \mathcal{E}_1^{\ddagger} \right) / RT \right] \qquad (62)$$

where $\frac{P_1}{P_6}$ is the ratio of probability of attack on atom 1 to atom 6, and $\mathcal{E}^{\ddagger}$ represents activation energy, one gets a rather conclusive result. Thus if the reaction is carried out at room temperature, RT=.6 Kcal./mole and if β is assumed to be in the neighborhood of 45 Kcal./mole,

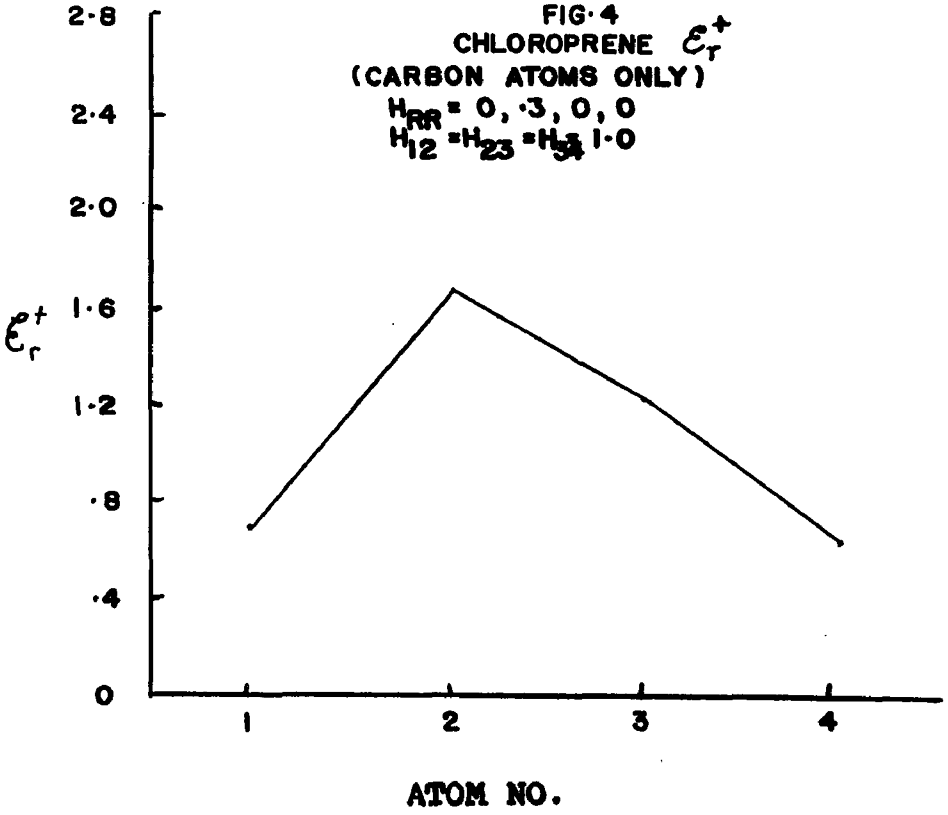
$$P_1/P_6 = \exp - [(\mathcal{E}_6^{+} - \mathcal{E}_1^{+})/RT] = \exp [(.69 - .65).45/6] \quad (63)$$
$$= 20/1$$

which shows an unquestionable predominance of electrophilic attack on atom 1.

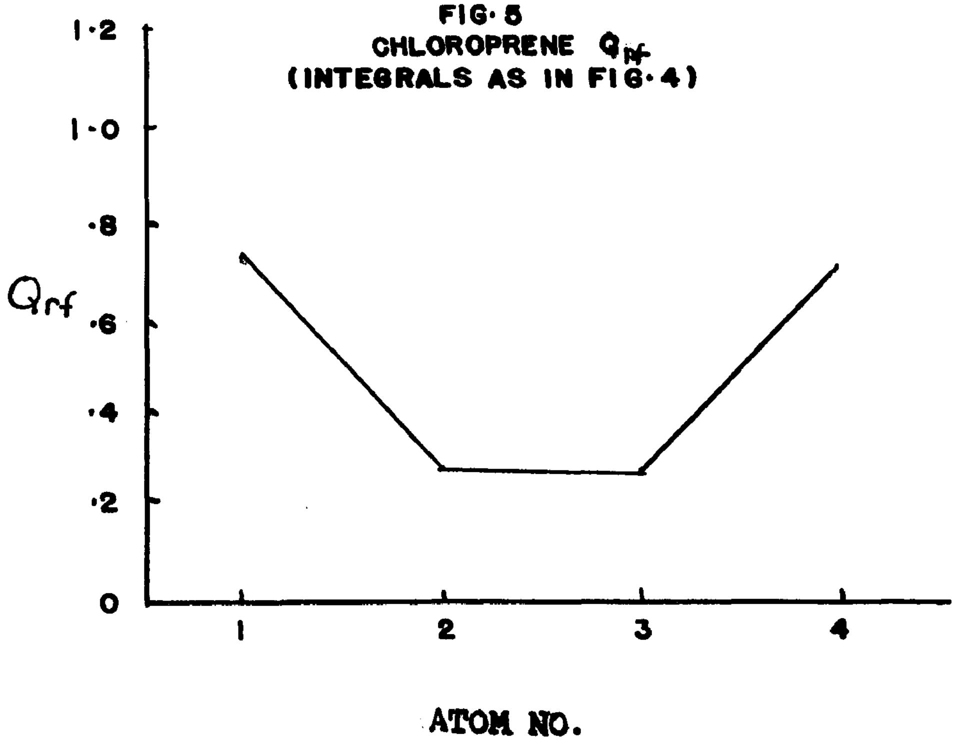
To return to the original discussion of isoprene reactivity, in terms of the SCF computation table 6 indicates the same trend as in propylene, where the β's involved in the second order conjugation are a bit unrealistic. The result again shows an unusual preponderance of charge on the methyl group, although the relative densities on atoms 1 and 6 are in the right order for the observed results. The general comparison of Q_{rr}'s shows this quantity for atoms 2 and 3 decidedly increasing, with 4, 5, and 6 decreasing in charge. Atom 1 changes only slightly. This molecule could be considered in more detail from the viewpoint of the integrals and reactivity parameters; however, it will be more worthwhile to consider a simpler system in detail which will be done when we come to the linear 5-atom complex of protonated butadiene.



$$\overset{1}{C}H_2{=}\underset{\underset{5}{Cl}}{\overset{2}{C}}{-}\overset{3}{C}H{=}\overset{4}{C}H_2$$



FIG·4
CHLOROPRENE $\mathcal{E}_r^+$
(CARBON ATOMS ONLY)
H_{RR} = 0, ·3, 0, 0
$H_{12} = H_{23} = H_{34}$ = 1·0



FIG·5
CHLOROPRENE Q_{rf}
(INTEGRALS AS IN FIG·4)

Table 7

Chloroprene Reactivity Parameters

Atom or Bond Number

	1	2	3	4	5
H_{rr}	0	.3	0	0	1.8
H_{rs}	1	1	1	.6	
Q_{rf}	.7006	.2671	.2659	.6976	.0688
ε_r	.8763	1.7491	1.3341	.8975	3.6419
ε_r^+	.6600	1.6667	1.2520	.6822	3.6207

In order to consider another way in which electrons may take part in conjugation see the results for chloroprene in table 7. The order in which the resonance integrals are listed is H_{12}, H_{23}, H_{34}, H_{25}. This system is viewed as having three occupied MO's, but in this case the chlorine atom supplies both electrons though it represents only one a.o. Since chlorine is more electronegative than carbon, the relative α value for it must be positive, as is the case of the adjoining carbon atom, because of the normal proximity effect in the inductive transmission of electronic charge. The value of α of 1.8 and .3 for Cl and its adjacent carbon atom, as well as the value of H_{25}, are chosen from a paper by Hayashi and co-workers.[27]

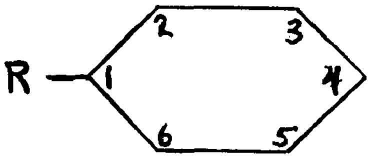
As with isoprene the differences between the parameters for the end carbon atoms is small (see Figs. 4, 5), but they are sufficient to show definite reactivity differences. It is interesting to note that in butadiene and the two substituted butadienes, isoprene and chloroprene, the frontier electron distribution over the four-carbon diene chain has about the same contour, and that the perturbation of the butadiene contour brought about by the methyl group and by the chlorine atom is relatively the same for the end atoms.

ANALYTICAL CONSIDERATIONS

Before considering the actual results of calculations on the activated complex it is well to consider the analytical method applied by Pilar[20] to the intermediate. (See p. 25f.) The form of this intermediate is considered in a somewhat different light than are following treatments and makes use of a 3 orbital system of 2 electrons. Thus either the proton or the halogen atom will remove from conjugation the elctrons of atoms 1 and 2 in butadiene, but together will contribute a group "atomic" orbital defined as Q_2 (p. 26).

This can now be viewed as an allylic system with relative resonance and coulombic integrals in accord with the electronegativity of the initial adduct relative to carbon. With hydrogen halide addition the H_2 is less electronegative, hence $H_{23} \leq H_{34}$ because of less bonding between atoms 2 and 3, and $H_{22} \leq H_{33}$ in units of β_0. Letting $H_{33}=H_{44}=0$, $H_{34}= \beta_0$, then H_{22} is called c in terms of β. So with proton addition $c \leq 1$ and $k \leq 1$, requiring nucleophilic attack on atom 2 as determined both by atom stabilization energies and frontier electron charge densities. One may refer to the above author's paper for the details of this analysis.

Pilar[28] has made further elaborations on this technique in applying it to aromatic electrophilic substitution in which he correctly predicts the directing influence of substituents. There are two k-values and 2 c-values for singly substituted benzene.

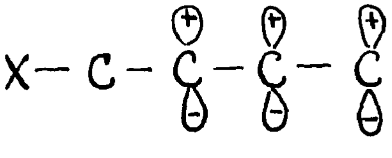


Thus $H_{11}=c_1$, $H_{22}=H_{66}=c_2$, $H_{12}=k_1$, $H_{23}=k_2$, and $H_{34}=H_{45}=1$. (64)

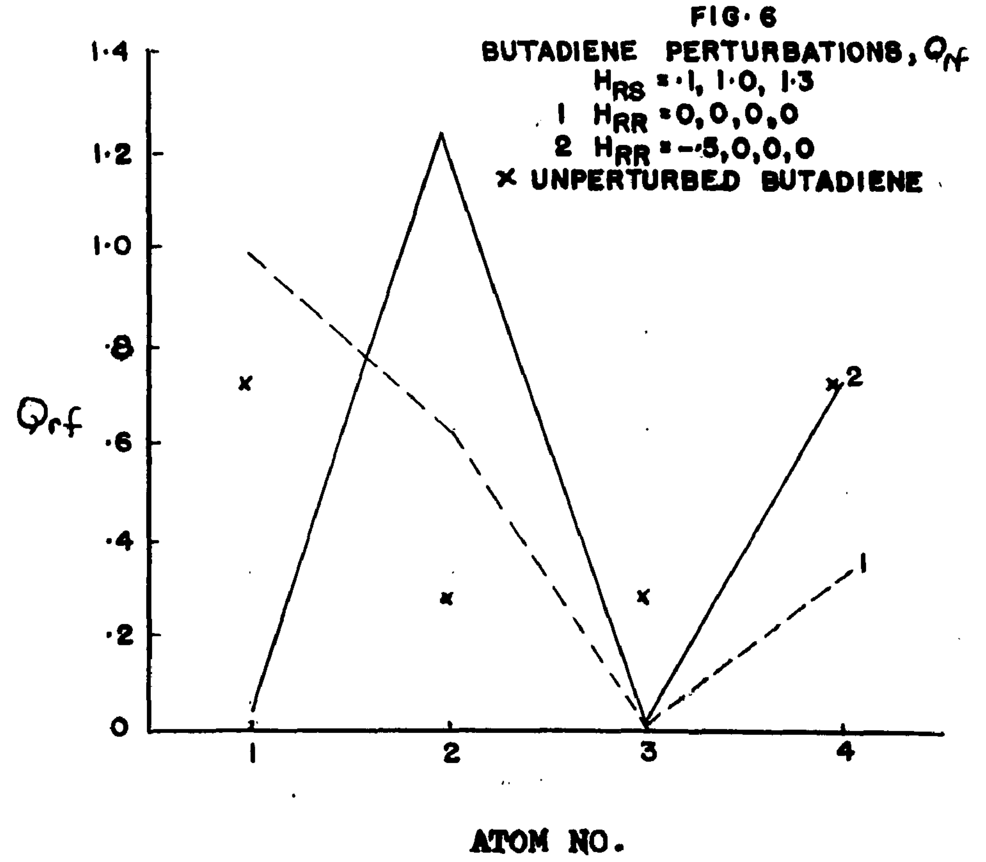
SIMPLE BUTADIENE PERTURBATION

Before going on to the detailed analysis of protonated butadiene including hyperconjugation, it is well to treat the activated complex first as a simple perturbation of the molecule, with the simultaneous removal of two electrons from conjugation. Thus the assumption is that there are four orbitals containing two electrons, neglecting hyperconjugation.

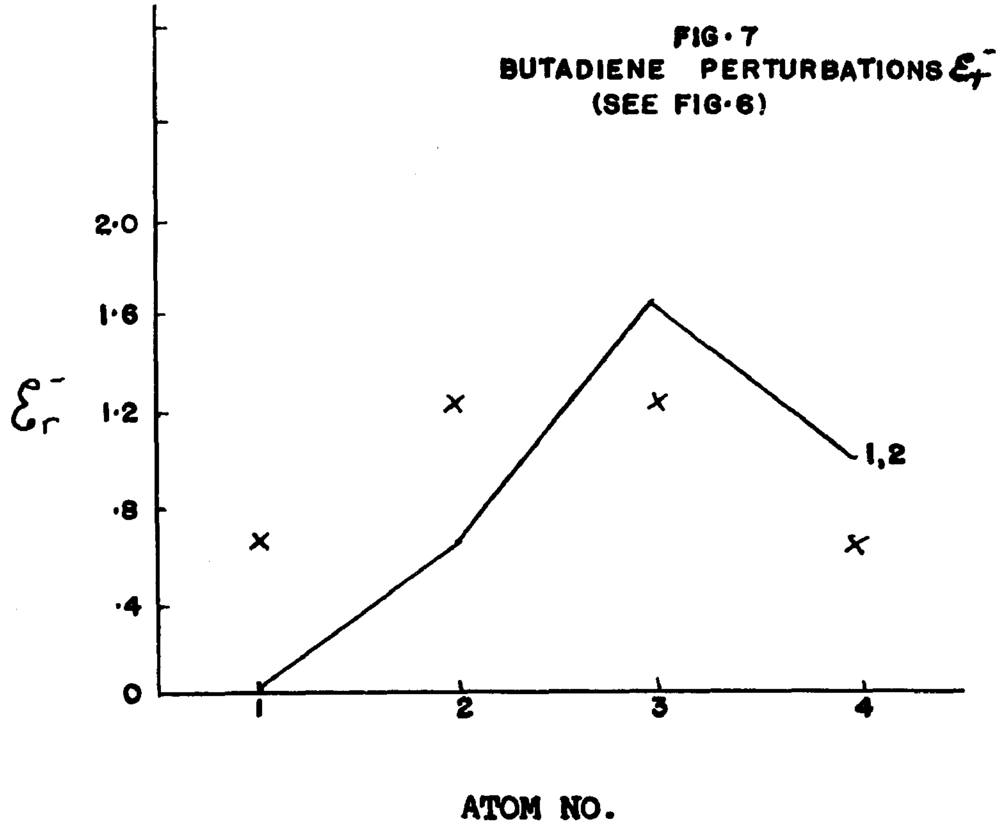
(Actually the activated complex should be expressed as



with X in this case representing a hydrogen atom and producing an orbital derived from a pseudo-heteroatom (see p. 50). Later it will be seen (p. 69ff) that a pi complex must be

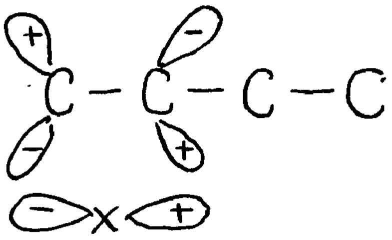


FIG·6
BUTADIENE PERTURBATIONS, Q_{rf}
H_{RS} = ·1, 1·0, 1·3
1 H_{RR} = 0,0,0,0
2 H_{RR} = −·5,0,0,0
× UNPERTURBED BUTADIENE



FIG·7
BUTADIENE PERTURBATIONS $\mathcal{E}_r^-$
(SEE FIG·6)

assumed if X is other than H, and the linear complex is invalidated. In other words, the orbitals would be represented as



This problem has been approached mathematically in two steps, first a perturbation expressed as a change in resonance integrals alone, then a simultaneous change in both resonance and coulombic integrals. The results are expressed in tables 8 and 9 and figures 6 and 7.

Table 8

H_{rs} Perturbation of Butadiene

Atom or Bond Number

	1	2	3	4
H_{rr}	0	0	0	0
H_{rs}	.1	1	1.3	
Q_{rf}	.9986	.6266	.0014	.3734
$\mathcal{E}_r$	.0023	.6130	1.6390	1.0282
$\mathcal{E}_r^+$	.0417	.6378	1.6391	1.0430

Table 9

Combined Perturbation of Butadiene

Atom or Bond Number

	1	2	3	4
H_{rr}	−.5	0	0	0
H_{rs}	.1	1	1.3	
Q_{rf}	.0468	1.2270	.0001	.7262
$\mathcal{E}_r$	.0014	.6122	1.6394	1.0288
$\mathcal{E}_r^-$	.0017	.6197	1.6394	1.0333

The lowest unoccupied level in this treatment is described in terms of ψ_2 as the determination of frontier charge densities for nucleophilic attack requires. This is also the frontier level for the butadiene molecule subjected to electrophilic attack, so it is possible to relate the shapes of the curves in figures 6 and 7 to butadiene directly. In general $\mathcal{E}_r^+ = \mathcal{E}_r^-$ for an alternant hydrocarbon, though in this case we are actually dealing with two different species.

Referring first to the perturbation by the resonance integrals, H_{12} being decreased brought about an increase in Q_{1f} and Q_{2f} as one might surmise because the electrons of the approaching ion would be occupied in the incipient bond and will exert an increased effect on frontier charge. Actually the situation is more complicated inasmuch as for nucleophilic attack we are describing an absence of electronic charge in the frontier level, in reality the positive charge present at an atom where the next two electrons from the negatively charged attacking reagent will most likely go. It is possible also to question this interpretation of H_{rs} vs. Q_{rf} effects on the basis of the linear correlation assumed for H_{rs} and P_{rs}. Hence if a small H_{rs} indicates <u>less</u> bonding, then P_{rs} should decrease, but if this is so, then the a.o. coefficients influencing P_{rs} must be diminished as well, resulting in a lessened charge density. This argument, however, loses sight of the fact that P_{rs} is based on all occupied levels, and though the frontier charges do go up on atoms 1 and 2, the bond order based on ψ_1 in this case) decreases, qualitatively, in accordance with the relationship we have assigned between this latter parameter and H_{rs}.

$$H_{12}=1.0, \quad P_{12}=.0114 \tag{65}$$

$$H_{12}=0.1, \quad P_{12}=.0087 \tag{66}$$

This relationship would apply even if we had considered a bond order based on $\psi_1 + \psi_2$ as is the case for butadiene.

$$H_{12}=1.0, \quad P_{12}=.8137 \tag{67}$$

$$H_{12}=0.1, \quad P_{12}=.2570 \tag{68}$$

In the opposite sense, as H_{34} is increased from 1.0 to 1.3 the frontier charge densities now decrease. A word of caution should be added, however, before too much confidence is placed in this simple, direct relationship among H_{rs}, P_{rs}, and Q_{rf}. We are dealing here with a very specific system, an even alternant hydrocarbon, and while the numerous results to be discussed in the next section also fit this expressed relationship of these parameters, even though it is a 5-atom system containing a pseudo heteroatom, sweeping generalizations are definitely to be avoided. This is especially true of quantitative speculations where the number of variables involved preclude such a desirable but unwarranted approach. One needs only to observe a plot of bond orders vs. resonance integrals to assure himself of this fact. One should hasten to add, however, that there is ample justification for using this "forced" linear dependence of H_{rs} on P_{rs} in most cases except with the $H_3 \equiv C$ bond for the iterative solutions.

Having compared the frontier charge densities for the first perturbation, one finds that the change in atom stabilization energies is parallel, but opposite in sign, reflecting as before a favoring of attack on atom 2 over atom 4.

In continuing to the second perturbation treatment of butadiene, that of simultaneously changing the resonance integrals and one coulombic integral, one sees a decisive change in the frontier charge density contour, particularly in the region of atom 1. (See figure 6.) This can be attributed to the change in electronegativity brought about by assigning α_1 the value of $-.5$, indicating less attraction for electrons. Because the proton is associated with atom 1, there is sufficient charge localization to partially remove it from conjugation, disallowing a more intensive positive charge at this position. Thus from figure 6, it is evident also that there is less ambiguity in that atoms 2 and 4 are the most heavily charged.

There is little apparent change in $\mathcal{E}_r^-$ over the entire molecule when one compares the two perturbations. In this case the ambiguity does arise since atom 1 in both instances has the lowest atom stabilization energy, whereas it is atoms 2 and 4 which should be most susceptible to nucleophilic attack. The order $\mathcal{E}_2^- < \mathcal{E}_4^-$ is correct, however. (See figure 7.)

PERTURBATIONS OF HYPERCONJUGATIVE PROTONATED BUTADIENE

In the last section was discussed an approach to the calculation of the reactivity criteria as a simple perturbation of the butadiene molecule. It is now of interest to study the criteria as a function of the same variables, but this time taking into account some explicit expression of the hyperconjugative phenomenon. The details of this study should be of interest insofar as they give us a better understanding of the effects which changing degrees of electronegativity and bonding have on the theoretically evaluated factors used in deciding upon reactivity in conjugated systems.

It will be seen that certain comparisons one makes can be related to the analytically determined polarizability as applied to neutral molecules by Coulson and Longuet-Higgins.[9] One may also see the connection of these computations with the work of Dewar[14]. Bear in mind, however, that one is treating not a molecule but a transition state complex, and that a degree of empirical chemical intuition is being used in assign-

Table 10

Coulombic Perturbations

$H_{12}=2.5$, $H_{23}=H_{34}=.7$, $H_{45}=1.0$

	Coulombic Integrals					Atom Stabilization Energies				
HBUT#*	1	2	3	4	5	1	2	3	4	5
23	0	0	0	0	0	2.4231	2.5930	.5555	1.2138	.8282
44	1	1	1	1	1	3.4231	3.5930	1.5555	2.2138	1.8282
24	-.2	0	0	0	0	2.2937	2.5908	.5557	1.2138	.8282
25	-.5	0	0	0	0	1.9619	2.5798	.5570	1.2136	.8282
26	-.8	0	0	0	0	1.7218	2.5596	.5594	1.2133	.8282
27	-.2	-.1	0	0	0	2.2268	2.4905	.5560	1.2138	.8282
28	-.8	-.1	0	0	0	1.7132	2.4537	.5605	1.2132	.8284
12	-.5	-.1	0	0	0	1.9563	2.4767	.5577	1.2136	.8283
29	-.5	-.3	0	0	0	1.9421	2.2792	.5587	1.2135	.8285
30	-.5	-.5	0	0	0	1.9243	2.0933	.5596	1.2134	.8287

---

*Appendix code numbers of computations.

Table 10 (cont.)

	Coulombic Integrals					Atom Stabilization Energies				
HBUT#	1	2	3	4	5	1	2	3	4	5
31	0	-.1	0	0	0	2.4227	2.4944	.5555	1.2139	.8282
32	0	-.3	0	0	0	2.4191	2.3060	.5552	1.2139	.8282
34	0	0	-.2	0	0	2.4233	2.5926	.3724	1.2103	.8227
35	0	0	.2	0	0	2.4233	2.5926	.7724	1.2103	.8227
33	0	0	0	-.2	0	2.4231	2.5930	.5543	1.0262	.8254
36	0	0	0	.2	0	2.4231	2.5930	.5543	1.4262	.8254
37	0	0	0	0	-.2	2.4230	2.5929	.5542	1.2084	.6462
38	0	0	0	0	.2	2.4230	2.5929	.5542	1.2084	1.0462
48	-.5	-.1	-.02	0	0	1.9564	2.4768	.5379	1.2134	.8280
49	.5	.1	.02	0	0	2.9564	2.6783	.5779	1.2134	.8280

FIG. 8
PROTONATED BUTADIENE $\mathcal{E}_r^-$
H_{11}, H_{33}, H_{55} PERTURBATIONS

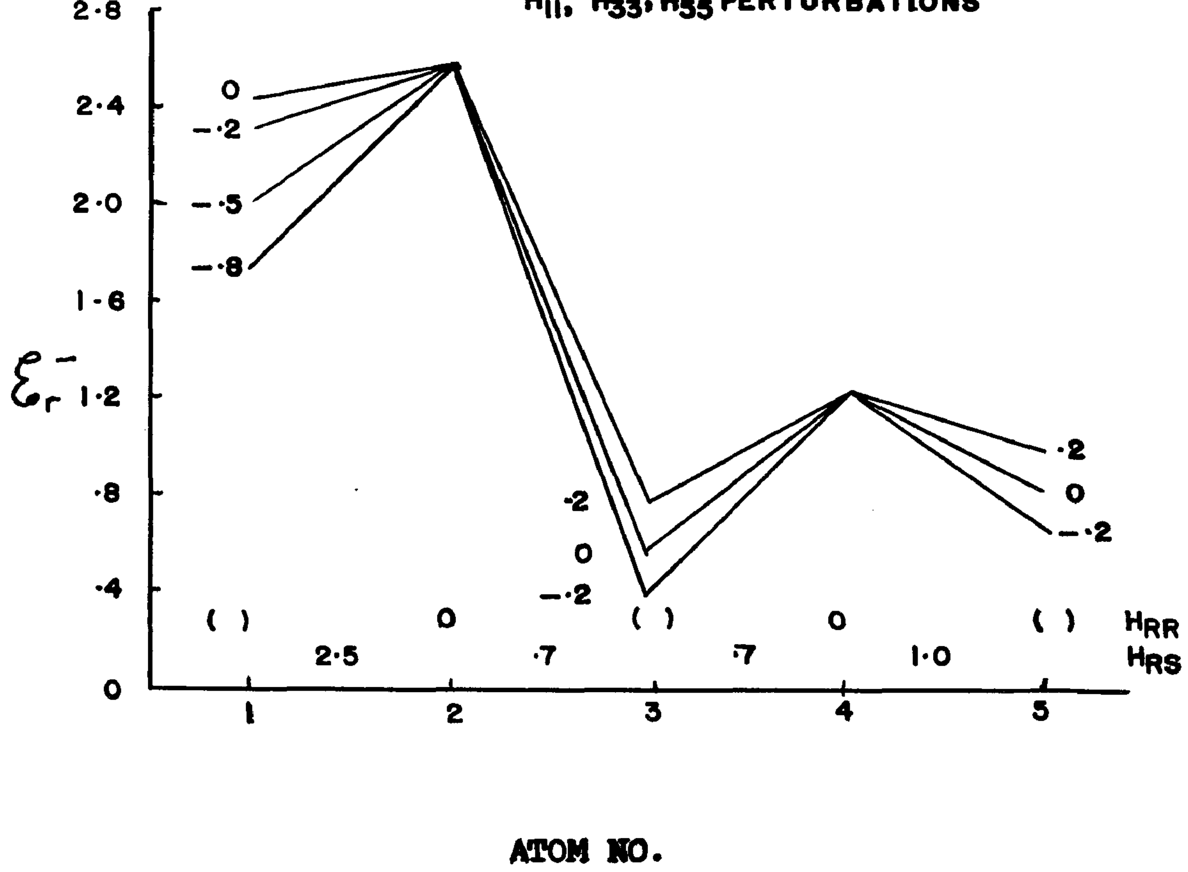


Table 11

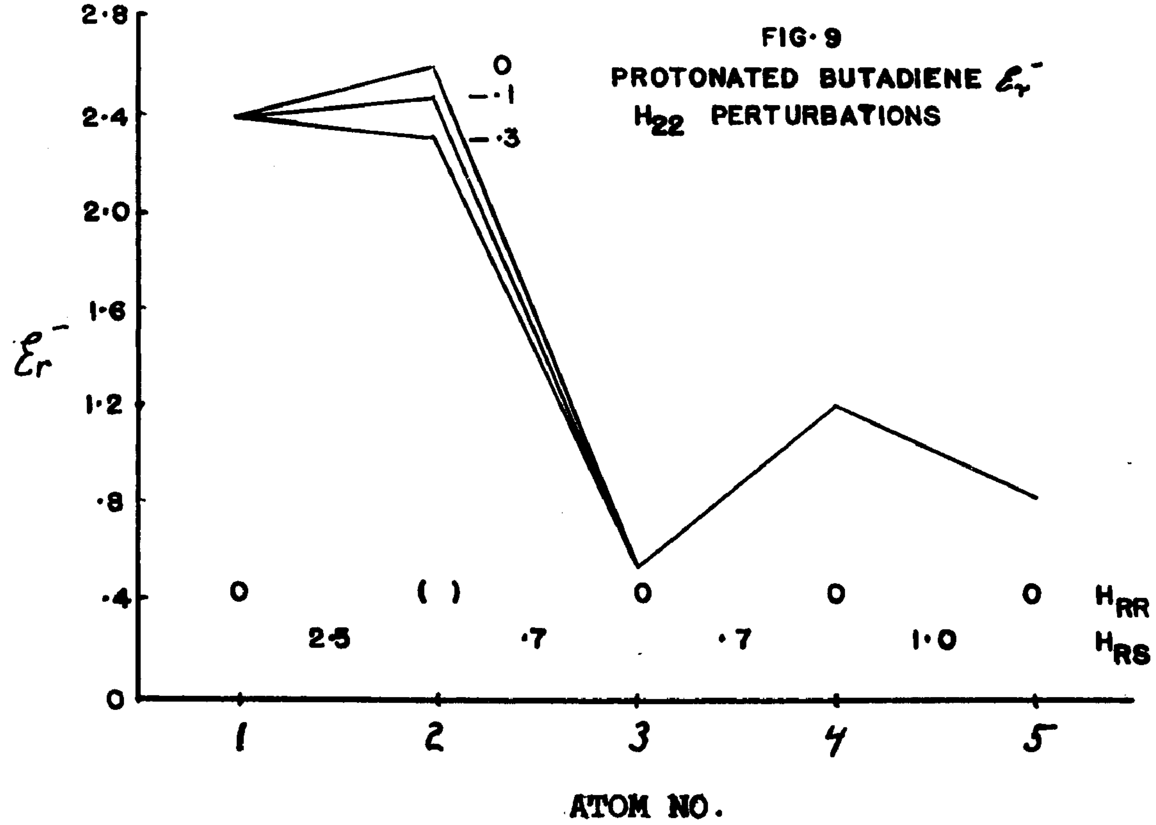
Coulombic Perturbations

$H_{12}=2.5$, $H_{23}=H_{34}=.7$, $H_{45}=1.0$

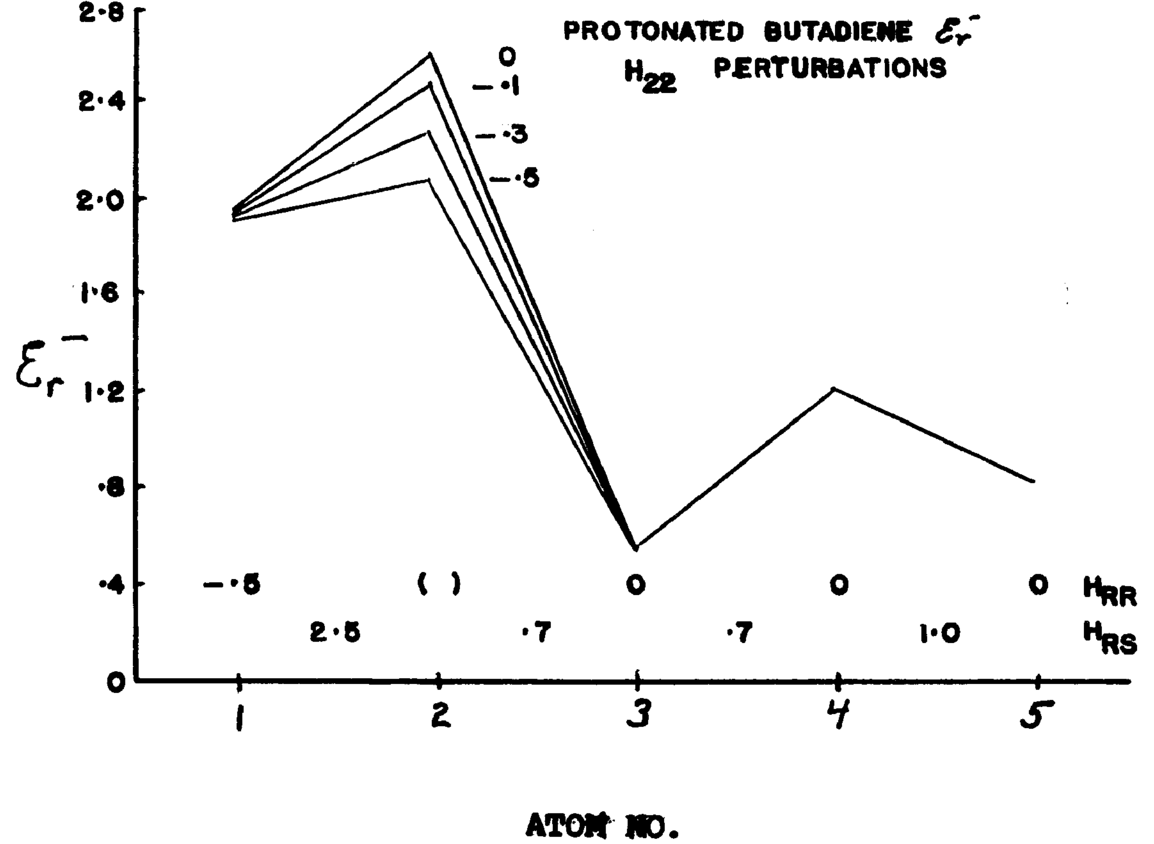
	Atom Energies					Frontier Electron Charge Densities				
HBUT#	1	2	3	4	5	1	2	3	4	5
23	2.4231	2.5930	.5555	1.2138	.8282	.1000	.0000	1.2752	.0000	.6248
44	3.3731	3.5930	.9179	2.2138	1.5158	.1000	.0000	1.2752	.0000	.6248
24	2.2299	2.5908	.5621	1.2138	.8313	.0999	.0001	1.2747	.0001	.6247
25	1.9632	2.5798	.5729	1.2136	.8360	.0994	.0036	1.2724	.0004	.6243
26	1.7238	2.5598	.5846	1.2133	.8406	.0985	.0091	1.2681	.0010	.6233
27	2.2273	2.4905	.5624	1.2138	.8314	.1005	.0006	1.2743	.0001	.6246
28	1.7152	2.4539	.5859	1.2132	.8409	.1007	.0093	1.2664	.0010	.6225
12	1.9563	2.4767	.5736	1.2136	.8361	.1008	.0036	1.2174	.0004	.6238
29	1.9434	2.2792	.5749	1.2135	.8365	.1038	.0037	1.2693	.0004	.6228
30	1.9257	2.0933	.5760	1.2134	.8368	.1069	.0038	1.2671	.0004	.6217

Table 11 (cont.)

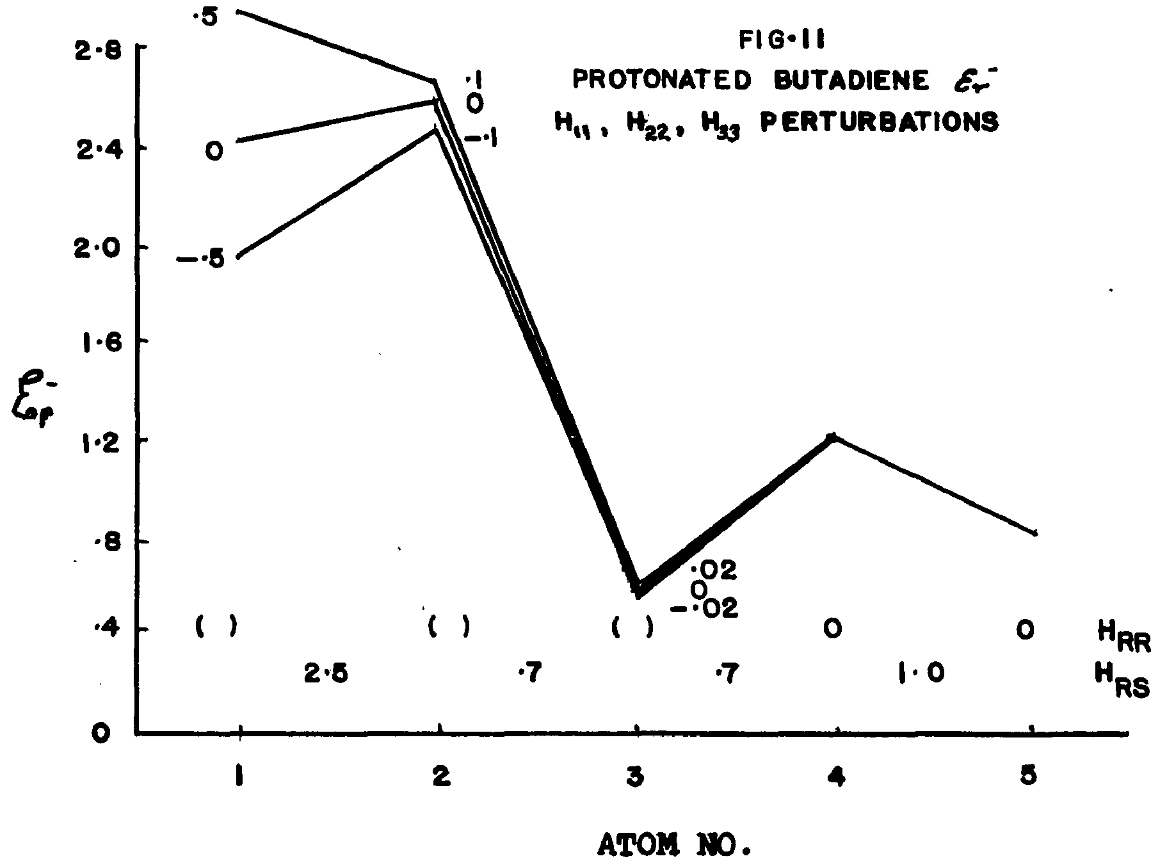
	Atom Energies					Frontier Electron Charge Densities				
HBUT#	1	2	3	4	5	1	2	3	4	5
31	2.4227	2.4944	.5555	1.2139	.8282	.1000	.0000	1.2752	.0000	.6248
32	2.4191	2.3060	.5552	1.2139	.8282	.1000	.0000	1.2752	.0000	.6248
34	2.4296	2.5927	.4520	1.2109	.8630	.0989	.0003	1.2552	.0102	.6354
35	2.4170	2.5926	.6928	1.2096	.7824	.0989	.0003	1.2552	.0102	.6354
33	2.4231	2.5930	.5543	1.0262	.8254	.1000	.0000	1.2752	.0000	.6248
36	2.4231	2.5930	.5543	1.4262	.8254	.1000	.0000	1.2752	.0000	.6248
37	2.4261	2.5929	.5938	1.2087	.6653	.1000	.0001	1.2744	.0117	.6139
38	2.4199	2.5929	.5146	1.2080	1.0271	.1000	.0001	1.2744	.0117	.6139
48	1.9583	2.4768	.5619	1.2135	.8398	.1005	.0034	1.2707	.0009	.6244
49	2.9545	2.6767	.5538	1.2134	.8162	.1005	.0034	1.2707	.0009	.6244



FIG·9
PROTONATED BUTADIENE $\mathcal{E}_r^-$
H_{22} PERTURBATIONS



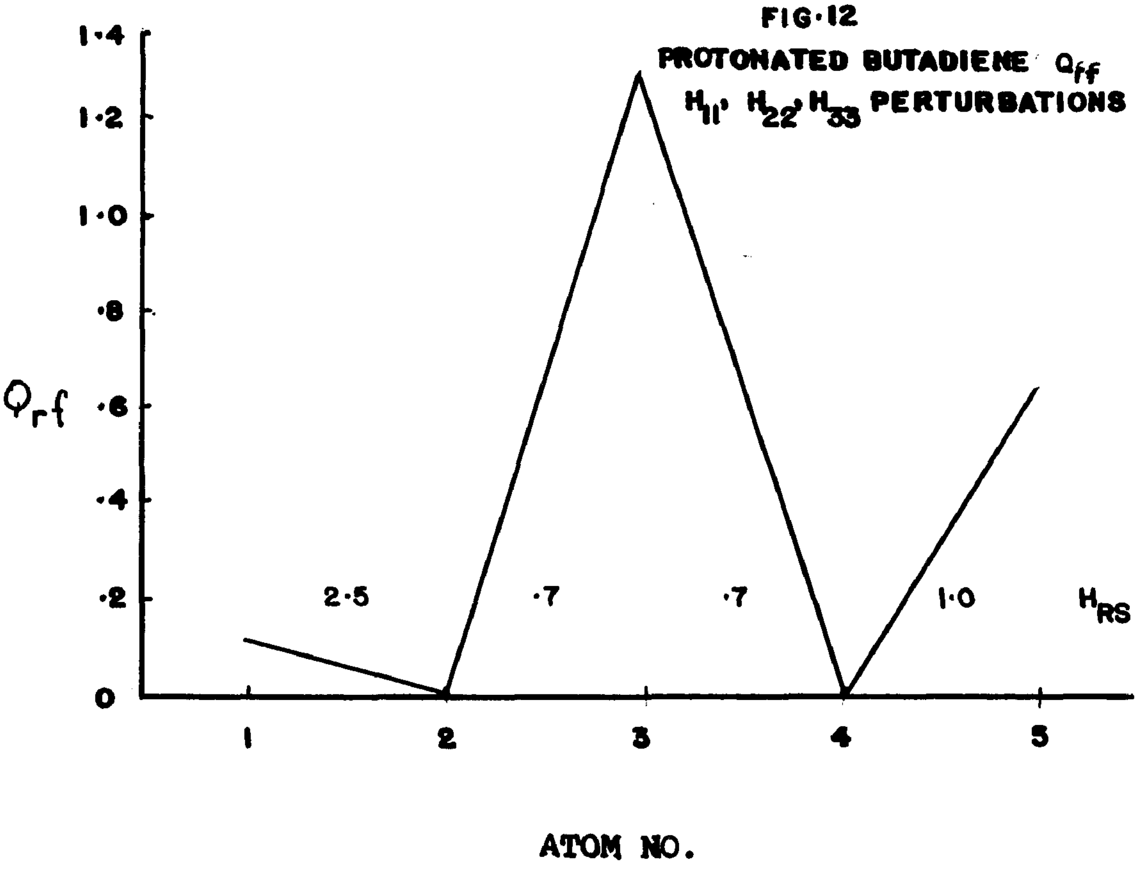
FIG·10
PROTONATED BUTADIENE $\mathcal{E}_r^-$
H_{22} PERTURBATIONS



FIG·11

PROTONATED BUTADIENE $\mathcal{E}_r^-$

H_{11}, H_{22}, H_{33} PERTURBATIONS



FIG·12

PROTONATED BUTADIENE Q_{ff}

H_{11}, H_{22}, H_{33} PERTURBATIONS ing the form of this complex.

The choice of a 5-atom complex, including the second order conjugation of the H_3 C group; is based on the work of Mulliken[13] and Coulson[8], as indicated earlier with the discussion of propylene (p. 29ff). It is possible to postulate other structures for this intermediate, such as a complex of the proton with one of the pi bonds. The existence of such a complex has been questioned on the basis of spectral data, however[26]. The choice, therefore, of a linear 5 a.o. system occupied by 4 electrons seems reasonable.

$$(\underset{1}{H_3} \equiv \underset{2}{C} - \underset{3}{CH} - \underset{4}{CH} - \underset{5}{CH_2})^+$$

Effect of changing electronegativity.

By carrying through series of actual calculations a qualitative idea may be gathered concerning the linking of changes in electronegativity with ease of nucleophilic attack. In this way one approaches an understanding of the polarizability of each position in the activated complex.

It should be noted that first order perturbation theory has not been applied to this problem. Such theory does not lend itself to presently considered reactivity criteria, namely frontier electron charge densities and atom stabilization energies.

Tables 10 and 11 list values of atom stabilization energies, atom energies, and free electron charge densities for a number of combinationsof coulombic integrals. The resonance integrals chosen for this series are 2.5, .7, .7 and 1.0 for bonds 1–2 through 4–5, and it will be shown that the generalizations to follow are not significantly dependent (at least in the range of values with which we are concerned) upon the latter parameters.

As one can see from table 10 and figures 8–11, there is a pronounced effect upon the values of $\mathcal{E}_r^-$ brought about by changes in the electronegativities of the atoms. It will be of interest, then, to deduce from this data any trends which could be important in determining reactivity in terms of $\mathcal{E}_r^-$ as well as Q_{rq}.

1. An increase in H_{rr} (in terms of β), reflecting an increase in electronegativity, causes an increase in $\mathcal{E}_r^-$. Thus the more electronegative is an atom in this system, the less susceptible is the atom to nucleophilic attack.

2. $\mathcal{E}_r^-$ are far more sensitive to changes in H_{rr} than are Q_{qr} .

The first generalization is immediately apparent from the first two entries in table 10 (HBUT# 23,44). In fact, the relationship in this case is direct and quantitative. We shall turn shortly to an investigation of the generality of the latter statement and to the tables and graphs for a qualitative as well as a semi-quantitative picture of the effects of coulombic perturbations, but first let us consider a brief clarification of the idea that a strong electron attraction at a given atom means less electrophilicity in a reaction with a negative ion.

Consider, for example, HBUT#23, 31 and 32, where H_{aa} changes from 0 to $-.1$ to $-.3$ respectively. The <u>total</u> charge density changes as a result from 1.00 to .98 to .94 (with an increase in Q_1, incidentally). A region of high electronegativity collects as much as it "needs" of the available electronic charge, and thus any other negatively charged particle will be repelled from this position relative to the others.

Referring to figure 8, one can see an almost quantitative correlation in the changes in $\mathcal{E}_r^-$ brought about by these H_{rr} variations. The results for atom 2 show the same relationship as depicted in figures 9 and 10. As to the degree of quantitative correlation, it is possible to make crude estimates of the effectiveness of a perturbation for an atom by noting the proportionate change effected in $\mathcal{E}_r^-$.

Thus for "atom" 1 it is informative to see that the changes involved in going from HBUT#31 to 27 to 12 to 28 are 98%, 90% and 81% effective, respectively. E.g., $(2.4227-2.2268)/.2=98\%$. It is apparent that the perturbation is not completely effective and that its effectiveness decreases with a decrease in electronegativity. For the most part these observations are also true for the other atoms.

The reason for the above behavior becomes apparent when the change in atom 2 is taken into account for part of this same series (HBUT#31–27). The .0039 change in $\mathcal{E}_2^-$ is nearly enough to account for the total perturbation. This is an approximate expression, then, of the inductive effect of the #1 atom perturbation on atom 2. One could also interpret this as a form of polarizability which is of course related to the inductive effect through the permanent polarization of electronic charge.

One might inquire, meanwhile, if the effects we have been discussing are dependent upon the particular values of the resonance integrals. From table 12 the effectivities of the H_{22} perturbations are 92%, 91% and 92% for the series HBUT#7–17, 9–15 and 10–16, respectively. For the moderate range of the H_{rs} variation this is not a very significant deviation.

Table 12

Resonance Integrals and Coulombic Perturbations

HBUT#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}	
7	−.5	−1.0	0	0	0	3	3	1	1	3.271
17	−.5	−.1	0	0	0	3	3	1	1	4.097
9	−.5	−1.0	0	0	0	3	2	1.5	1	2.628
15	−.5	−.1	0	0	0	3	2	1.5	1	3.448
10	−.5	−1.0	0	0	0	3	3	1.5	1	3.233
16	−.5	−.1	0	0	0	3	3	1.5	1	4.060

The second generalization involves a comparison of the perturbation results of e_r^- and Q_{rf}. From table 11, it is evident that frontier electron charge densities are relatively immune to even large changes in electronegativity. Consequently figure 12 approximately represents the entire range of values of Q_{rf} depicted in table 11.

To understand the meaning for this relative immunity, consider the definition for $\mathcal{E}_r^-$.

$$\mathcal{E}_r^- = 2 \sum_j^{occ.} C_{rj} E_j + \sum C_{rf}^2 \tag{69}$$

is linear in <u>both</u> C_{rj}^2 and E_j, whereas Q_f is more independent of the energy levels. This is especially true when the scaling of the matrix is such that the frontier orbital eigenvalue is appreciably smaller numerically than are the other energies, as is the case in nearly all the HBUT series. Referring to table 13 and examining the effects of the perturbations on the eigenvalues, E_3 is seen to be smaller by two orders of magnitude than the total pi electron energy, $2(E_1+E_2)$. Judging from this it would also be expected that the effect of the frontier level upon $\mathcal{E}_r^-$ is small, an observation confirmed by a comparison of tables 10 and 11. Hence atom energies can also conceivably be used as means for predicting chemical reactivity.

Table 13

Eigenvalues

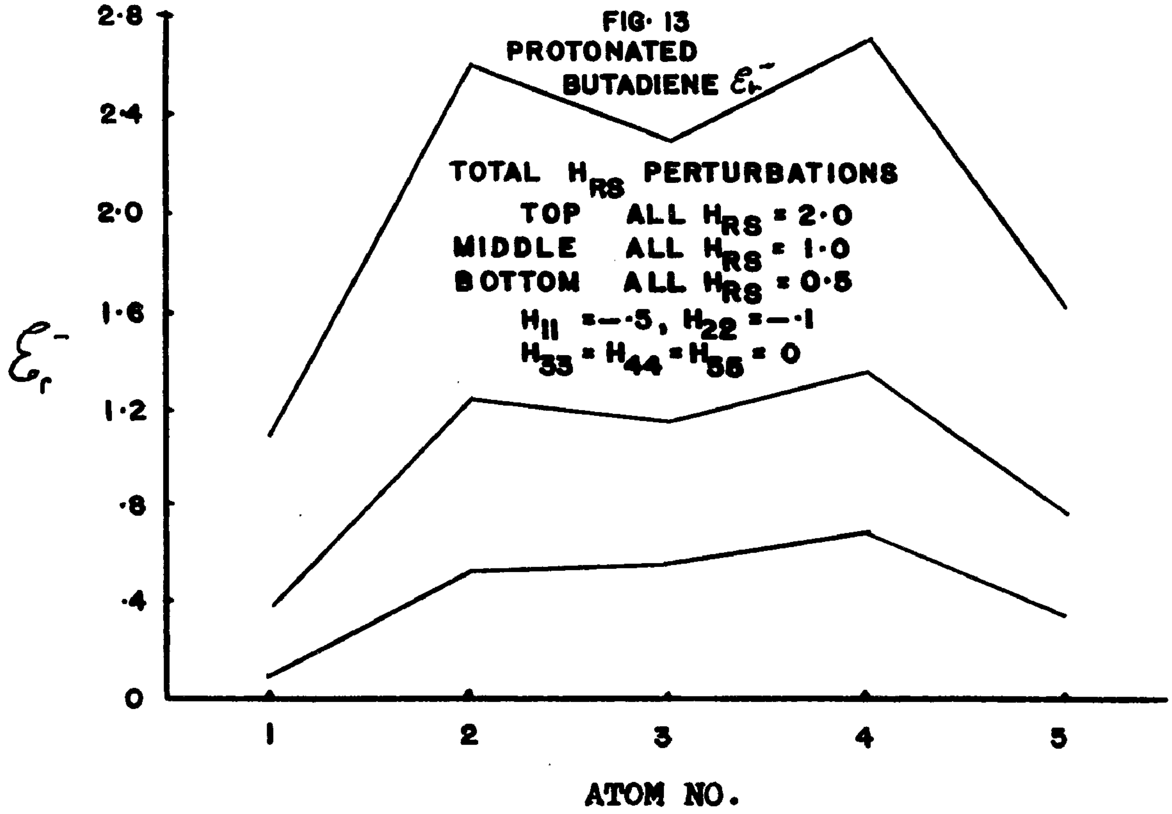
HBUT#	E_1	E_2	E_3	E_4	E_5
12	2.3378	1.1910	−.0251	−1.2106	−2.8931
29	2.2350	1.1887	−.0255	−1.2108	−2.9874
30	2.1365	1.1861	−.0259	−1.2110	−3.0857
37	2.6048	1.1386	−.0621	−1.2763	−2.6050
38	2.6050	1.2763	.0621	−1.1386	−2.6048
23	2.6049	1.2019	−.0000	−1.2019	−2.6049
31	2.5558	1.2015	−.0000	−1.2024	−2.6549

Comparing HBUT#37 and 38 it is seen that a change in sign of the coulombic integral reverses the order of the eigenvalues with the result that the sign of the frontier level is changed. Finally, it has been observed that when $H_{22}=H_{33}=H_{55}=0$ the frontier eigenvalue is extremely small, suggesting a non-bonding state (HBUT#23, 31). It is not surprising that atom stabilization energies, depending as they do on the two occupied levels, are affected considerably more by coulombic perturbations than are frontier electron densities.

Effect of resonance integral variations.

As H_{rr}'s were discussed in the previous section, attention now will be directed toward H_{rr}'s and their influence on the reactivity parameters. The effect of varying H_{rs} uniformly as in figure 13 shows an increase of all $\mathcal{E}_r^-$ together with an enhancement of the differences in the respective values. As usual the alternating character of $\mathcal{E}_r^-$ displays itself, caused by the high negative coulombic perturbation of the first "atom" with $\mathcal{E}_1^-$ lowest.

The results for the Q_{rf}'s are depicted in figure 14 for all $H_{rs}=.5$ and for $H_{rs}=1.0$. The same trend in electrophilicity exists as with the $\mathcal{E}_r^-$'s. Unlike the conclusion reached in the last section, that coulombic perturbations are relatively independent of the absolute β values, it is already evident that "atom" 1 with $H_{11}= -.5$ is affected most strongly by a resonance integral perturbation. This fact can be of importance in evaluating the proper parameters to be chosen in MO calculations of reactivity. Notice that in the case of HBUT#3-5, the order of likelihood of nucleophilic attack is


FIG· 13

PROTONATED BUTADIENE $\mathcal{E}_r^-$

TOTAL H_{RS} PERTURBATIONS

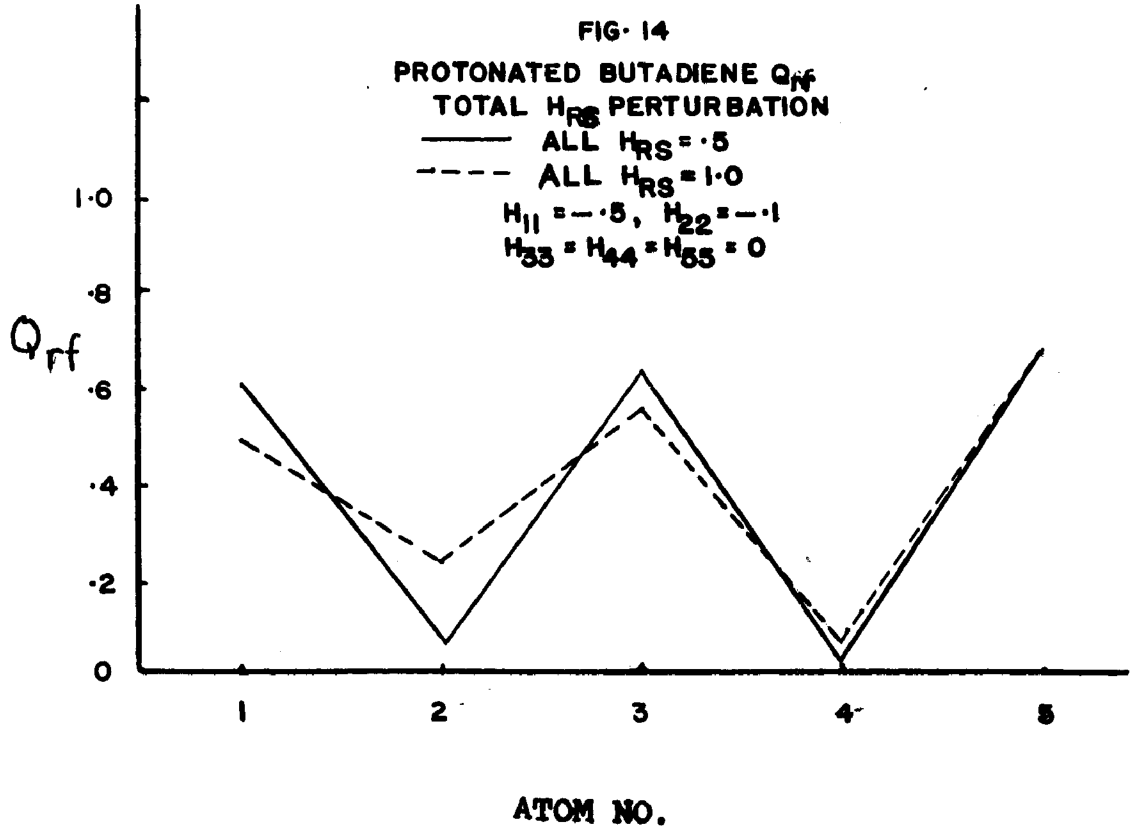
TOP ALL $H_{RS} = 2{\cdot}0$

MIDDLE ALL $H_{RS} = 1{\cdot}0$

BOTTOM ALL $H_{RS} = 0{\cdot}5$

$H_{11} = -{\cdot}5$, $H_{22} = -{\cdot}1$

$H_{33} = H_{44} = H_{55} = 0$


FIG· 14

PROTONATED BUTADIENE Q_{rf}

TOTAL H_{RS} PERTURBATION

——— ALL $H_{RS} = {\cdot}5$

– – – – ALL $H_{RS} = 1{\cdot}0$

$H_{11} = -{\cdot}5$, $H_{22} = -{\cdot}1$

$H_{33} = H_{44} = H_{55} = 0$

atom #1 $> 5 > 3$ for $\mathcal{E}_r^-$ and $5 > 3 > 1$ for Q_{rf}.

In this regard it is interesting to investigate at least superficially the mathematical requirements of this system, applying equally as well to linear molecules or other ions with odd numbers of molecules. To do this one writes the pertinent secular equations (70 and 71) for protonated butadiene as a hyperconjugative activated complex. Empirically atom 3 is the site of predominant attack by a halide ion; therefore, it is necessary to find the proper values of the resonance and coulombic integrals which express this fact. Moreover, since one may refer to the literature for an initial approximation of H_{11}, H_{22}, H_{12} and H_{23}, attention can be focused mainly on H_{33}, H_{44}, H_{55}, H_{34} and H_{45}. The secular equations are:

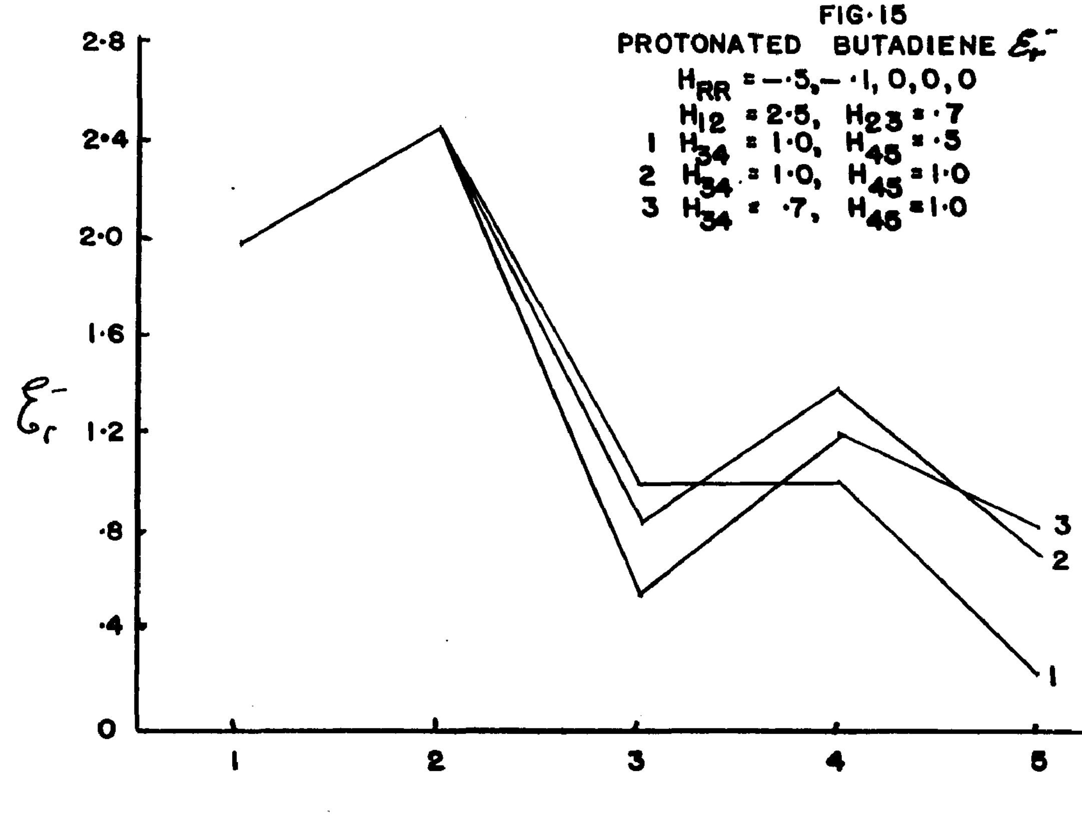
$$C_3(H_{34}) + C_4(H_{44}-E) + C_5(H_{45}) = 0 \qquad (70)$$

$$C_4(H_{45}) + C_5(H_{55}-E) = 0 \qquad (71)$$

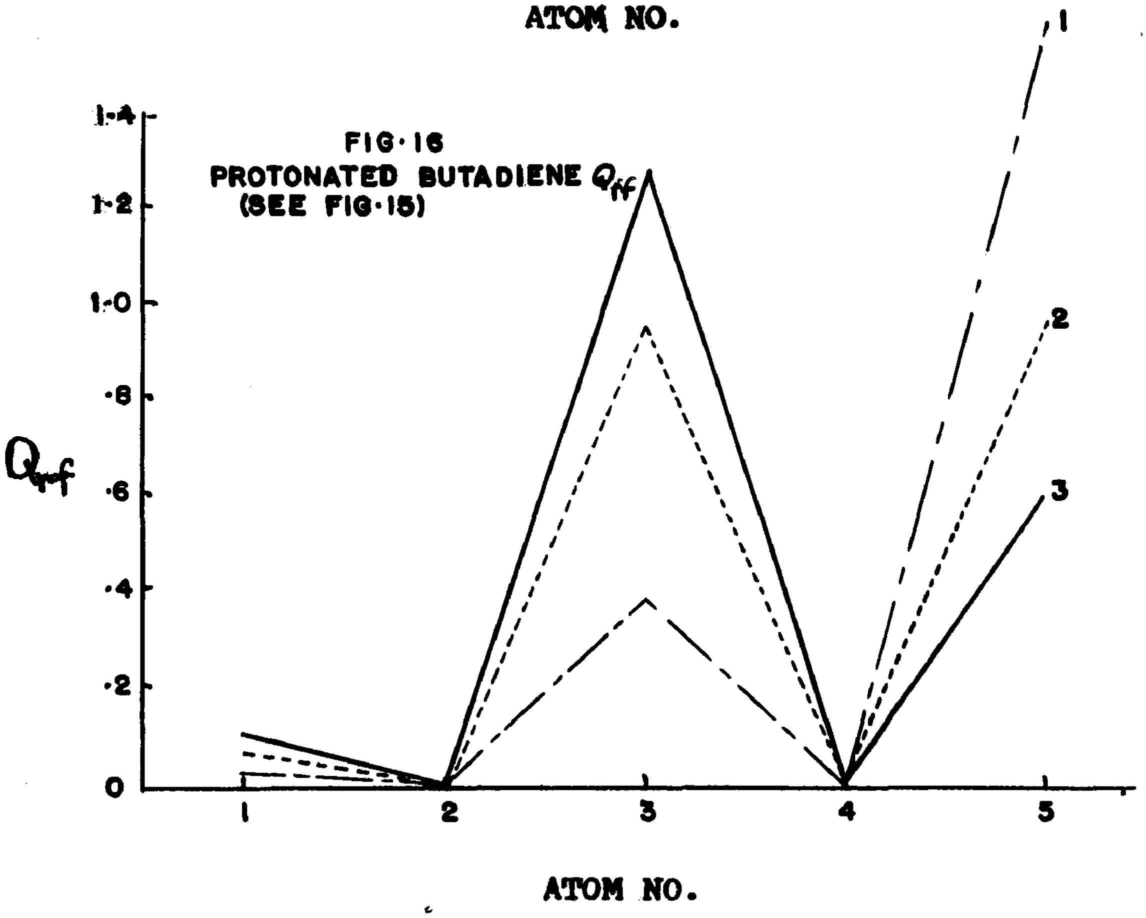
from which one may derive, assuming $H_{33}=H_{44}=H_{55}=0$,

$$C_5/C_3 = \frac{H_{34}\ E^2}{(E^2-H_{45}^2)\ H_{45}} - \frac{H_{34}}{H_{45}} \qquad (72)$$

It will now be possible to make an educated guess as to the relative values of the resonance integrals H_{34} and H_{45} which meet the experimental requirements of #3 atom nucleophilic attack. Furthermore, it will be convenient (and reassuring) to see that the same relative values apply to Q_{rf}



FIG·15
PROTONATED BUTADIENE $\mathcal{E}_r^-$
$H_{RR} = -\cdot5, -\cdot1, 0, 0, 0$
$H_{12} = 2\cdot5,\ H_{23} = \cdot7$
1 $H_{34} = 1\cdot0,\ H_{45} = \cdot5$
2 $H_{34} = 1\cdot0,\ H_{45} = 1\cdot0$
3 $H_{34} = \cdot7,\ H_{45} = 1\cdot0$



FIG·16
PROTONATED BUTADIENE Q_{rf}
(SEE FIG·15)

as well as $\mathcal{E}_r^-$.

Considering atom stabilization energies one makes the initial assumption that the frontier level contributes negligibly to these quantities, at least for present purposes. It is reasonable that in a 5 atom system with a small total coulombic energy that the third (frontier) level will approach zero. It also turns out to be negative when the total coulombic energy is negative. It is possible, then, to restrict ourselves to consideration of E_1 and E_2, the occupied levels, in ascertaining the effect of the resonance integrals on $\mathcal{E}_r^-$, perhaps now more specifically $\mathcal{E}_r^-$.

The criterion for judging the relative E_r's requires $E_3 < E_5$, and is based on C_3 and C_5 for the occupied levels where now $|C_3| < |C_5|$. Also important is the symmetry of the a.o. coefficients, noted as follows according to sign for HBUT#3, 4, 5.

	C_1	C_2	C_3	C_4	C_5
E_3	+	+	−	−	+
E_2	+	+	+	−	−
E_1	+	+	+	+	+

We may now deduce by inspection of equation (72) that for E_1 and E_2, both being positive, that C_5/C_3 approaches infinity as H_{45} approaches the value of E. Hence H_{45} should be large (up to E) and will have a greater effect on $\mathcal{E}_r$ and $\mathcal{E}_r^-$ than H_{34}. The relative magnitude of H_{34} desirable is not determinable by inspection since changes in this integral will bring about opposing effects in the two terms of (72) for E_1. Chemical intuition indicates, however, that there should be only a small localization of electronic charge between atoms 3 and 4 compared to that between atoms 4 and 5 for atom 5 to predominate in charge density and hence yield a high value of C_5/C_3.

Turning to the effects of these integrals on the frontier electron charge densities, we find that now it is necessary to prove that a low value of C_5/C_3 will result from a high value of H_{45}. In this case we refer again to the fact that under the conditions we have chosen E_3 will be negative and relatively small in magnitude. It is apparent both from the requirement that C_5/C_3 be negative for the frontier level and from equation (72) that a large value of H_{45} and a small value of H_{34} will indeed bring about the ratio favored for 1,2 addition to butadiene.

These features of the reactivity parameters are well borne out by figures 15 and 16 where the atom stabilization energies and frontier electron charge densities are depicted for HBUT#42, 40 and 12, involving first a change in H_{45} from 15 to 1.0 then a change in H_{34} from 1.0 to 0.7 respectively.

<u>Iterative treatment of the activated complex.</u>

On page 27 was discussed an iterative technique for arriving at better values of the resonance integrals, as well as more realistic reactivity parameters. This method as applied to propylene (p.32) with hyperconjugation gave rather unreasonable results in view of the resultant resonance integral for the $H_3 \equiv C$ bond. In a series of SCF determinations an attempt has been made to correct this defect and study the sensitivity of the reactivity criteria to the relative hyperconjugative resonance integral.

Table 14

SCF Protonated Butadiene , Q_{rf}

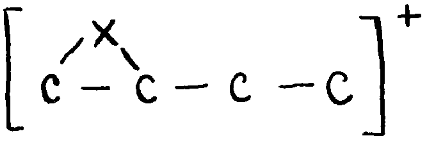
	H_{12}/H_{23}		1	2	3	4	5
1	2.0/.7	$\mathcal{E}_r^-$	1.6649	2.2242	.8093	1.2909	.7009
2	2.5/.7	$\mathcal{E}_r^-$	2.1445	2.6717	.7849	1.2959	.6863
3	3.0/.7	$\mathcal{E}_r^-$	2.6200	3.1259	.7676	1.3192	.6777
1		Q_{rf}	.1217	.0055	.9802	.0009	.8917
2		Q_{rf}	.0785	.0025	.9906	.0004	.9280
3		Q_{rf}	.0546	.0013	.9951	.0002	.9487

As table 14 indicates, an increase in the ratio of H_{12}/H_{23} from 2.0/.7 to 2.5/.7 to 3.0/.7 causes a nearly proportionate increase in $\mathcal{E}_1^-$ and $\mathcal{E}_2^-$. This parallels the results already obtained and depicted in figures 15 and 16 for H_{34} and H_{45}. The trend in Q_{rf} is down slightly and Q_{5f} is up slightly for this increase in the resonance integral ratio.

The cause of the shift in reactivity is of course due to the change in the resonance integrals used in their evaluation. In this series the input values of H_{rs} were 2.5, .7, 1.0, 1.0 for H_{12} to H_{45} respectively, and it is interesting to note that the value of H_{34} decreased somewhat through iteration, in keeping with what we believe to be the true picture of the relative bonding between atoms 3 and 4 vs. atoms 4 and 5. Also of interest is the fact that iteration caused an increase in H_{12} for the 2.5/.7 ratio from the input value of 2.500 to 2.688. It is difficult to say whether this trend leads us closer or not to the true picture of $H_3 \equiv C$ bonding in the activated complex.

The next question concerns the reliability of the iterative method. That is, can one be sure that self-consistency is independent of input data? The test of this reliability is illustrated by the sample program in the appendix. The values from the illustrative program are based on input resonance integrals of 2.5, .7, .7, 1.0 for the first run and 1, 1, 1, 1 for the second. In each case there were 5 iterations at a self-consistency of .0001 β_o .

THE PI COMPLEX AND THE HALONIUM ION



On page 50 it was mentioned that a less likely form for the intermediate in the hydrohalogenation of butadiene is the pi complex. As a matter of theoretical interest, however, a determination of the reactivity parameters of this complex was made. Moreover, though there is evidence that the proton pi complex may not be favored, it is perhaps more likely that in halogenation such a complex or "halonium" ion may form.[29] The results of these determinations are indicated in table 15 where atom stabilization energies are listed for an

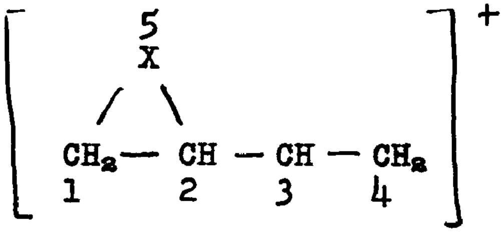


Table 15

Pi Complex and Halonium Ion

	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{15}	H_{25}					
HPi	−.2	−.2	0	0	−.2	2.0	.7	1.0	2.0	2.0	2.4954	2.5752	.7475	.5240	2.4956
XPi1	.2	.2	0	0	1.0	.8	.7	1.0	.5	.5	.8886	1.1577	1.1864	.8890	1.8992
XPi2	.1	.1	0	0	1.0	.8	.7	1.0	.5	.5	.8006	1.0615	1.1868	.8929	1.9262
XPi3	.1	.1	0	0	.5	.8	.7	1.0	.5	.5	.8774	1.1087	1.1861	.9101	1.0390
XPi4	.2	.2	0	0	1.0	.8	.7	1.0	.6	.6	.9310	1.1839	1.1886	.8963	1.9549
XPi5	.2	.2	0	0	1.0	1.0	.7	1.0	.5	.5	1.0714	1.3229	1.1737	.8954	1.8435

assumed 5 atom 4 electron species.

It may be possible to select "better" values for the integrals of the proton pi complex than those indicated, as for example a lower H_{12}. It is difficult as yet, however, to ascertain a reasonable pattern of resonance and coulombic integrals and one could speculate to quite widely differing conclusions. Suffice it to say that under the postulated electronic conditions the nucleophilic stage of hydrohalogenation results in attack on the 4 atom in contradiction to observed fact. Perhaps this could be used as an argument against the existence of the proton pi complex.

With the determinations attempting to similate the conditions of the halonium ion, however, one has a better chance of speculating, since it is known that under kinetic control chlorination yields the 1,2 addition product predominantly, whereas bromination yields mainly the 1,4 addition product.[31]

Of the perturbations indicated in table 15, then, which are directed to the conditions of chlorination and which to bromination? Do the results agree with known bonding conditions? Certain observations and conclusions follow.

1. Increase in electronegativity of atom 5 enhances the probability of #1 atom attack, in agreement with the fact that Cl likes electrons more than does Br. It is interesting too that the first Cl atom is apparently more tightly bound to the second carbon than the end carbon.

2. Increase in H_{15} and H_{25} would be in accordance with a decrease in bond distance such as would be encountered

in changing from a Br to a Cl atom. Unfortunately this incorrectly predicts preference of attack on atom 4. It is conceivable that inductive (electronegativity) effects are more powerful than resonance interactions, in which case observation 1 takes precedence over the present observation.

3. The greater the electronegativity of carbons 1 and 2, the greater the chance of #4 atom attack, in discordance with the expected proximity effects of the more electronegative chlorine.

4. Increasing H_{12} enhances the possibility of 1,4 addition. <u>A posteriori</u> judgment makes this seem quite reasonable, since H_{12} will be less perturbed, thus favoring a higher value.

An alternative approach in the case of butadiene would be to consider the halogenation intermediate a 4 electron linear ion similar in structure to the hyperconjugative protonated butadiene with 5 atoms. In this case, however, no conjugation can take place with X.

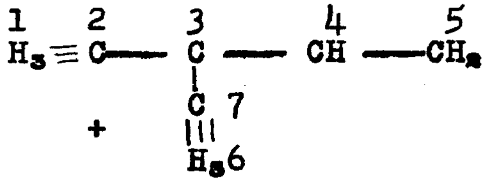
$$\left[X-CH_2-CH-CH-CH_2 \right]^+$$

When X is chlorine, $H_{11}=1.8$, $H_{22}=3$, $H_{33}=H_{44}=H_{55}=0$, and $H_{12}=6$, $H_{23}=1.0$, $H_{34}=.7$, $H_{45}=1.0$. With this input data the results show that $\mathcal{E}_5^- = .7302$, while $\mathcal{E}_3^- = 1.0418$, indicating a predominance of 1,4 addition in discordance with experiment. However, the same system with resonance and coulombic parameters similating a bromination the results are $\mathcal{E}_5^- = .8094$, and $\mathcal{E}_3^- = 1.0332$, in agreement with experiment. In the latter case $H_{11}=1.0$, $H_{22}=.2$, $H_{33}=H_{44}=H_{55}=0$, $H_{12}=.5$, $H_{23}=1.0$,

$H_{34}=.7$ and $H_{45}=1.0$. Thus the results of this type of treatment are perhaps less conclusive than are those involving the pi complexes.

PROTONATED ISOPRENE AND PROTONATED CHLOROPRENE

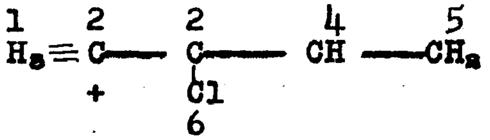
The reactivity of isoprene can be approached on the same basis as that of butadiene, with the proton being attached to carbon 1 in the molecule depicted on page 36. Using reasonable values for the resonance and coulombic



$$\overset{1}{H_3}\equiv\overset{2}{C}-\underset{\underset{\underset{H_3\,6}{|||}}{C\;7}}{\overset{3}{C}}-\overset{4}{CH}-\overset{5}{CH_2}\quad +$$

integrals, namely $H_{22}=H_{66}=-.5$, $H_{22}=H_{77}-.1$, $H_{33}=H_{44}=H_{55}=0$, $H_{12}=H_{67}=2.5$, $H_{23}=H_{37}=H_{34}=.7$, $H_{45}=1.0$, we find that $\mathcal{E}_3^-=.7054$, and $\mathcal{E}_5^-=.8360$, indicating a predominance of attack on atom 3. This is in accord with the experimental results of Jones and Chorley.[32]

Chloroprene, with a proton initiated attack on atom 1, (table 7) will further react with the bromide ion at position 5 of the activated complex according to Petrov.[33]



$$\overset{1}{H_3}\equiv\overset{2}{C}-\underset{\underset{6}{Cl}}{\overset{2}{C}}-\overset{4}{CH}-\overset{5}{CH_2}\quad +$$

Considering this to be a 4 electron, 6 atom system with integrals $H_{11}=-.5$, $H_{22}=-.1$, $H_{33}=.3$, $H_{44}=H_{55}=0$, $H_{66}=1.8$, $H_{12}=2.5$, $H_{23}=H_{34}=.7$, $H_{45}=1.0$ and $H_{36}=.6$, secondary attack of the halogen ion is on atom 5 ($\mathcal{E}_5^-=.4267$, $\mathcal{E}_3^-=.8978$), also in agreement with experiment in the kinetically controlled process.

SUMMARY

This work has been devoted to a theoretical study of simple addition reactions with butadiene and certain substituted butadienes. The method employs simple LCAO-MO theory. One addition reaction studied is the hydrohalogenation of butadiene. Assuming a linear carbonium ion type complex for the first step of the reaction, the method used suffices to predict qualitatively the results of this reaction if proper account is taken of hyperconjugation.

If one considers a linear carbonium ion derived from butadiene and bromine, the results of bromination are correctly predicted. In this case no conjugation is possible between the attached bromine atom in the transition state and the remainder of the ionic intermediate.

On the other hand, chlorination can be explained on the basis of a halonium ion pi complex. This type of structure requires the use of a suitable degree of both conjugative and inductive effects.

Lastly, hydrohalogenation of substituted butadienes such as isoprene and chloroprene can also be successfully treated in the prescribed manner in predicting reactivity.

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APPENDIX

I. Definitions of Symbols Used

Ψ	Total molecular wave function.
ψ_j	One electron molecular wave function of level j.
ϕ_r	One electron atomic wave function of atom r.
τ	General spatial coordinate.
E_j	Eigenvalue or electronic energy of level j.
H	Hamiltonian operator.
$\alpha_r = H_{rr} = \int \phi_r H \phi_r d\tau$	Coulombic integral.
$\beta_{rs} = H_{rs} = \int \phi_r H \phi_s d\tau$	Resonance integral.
$S_{rs} = \int \phi_r \phi_s d\tau$	Overlap integral.

C_{rj} = Eigenvector or atomic orbital coefficient of atom r.

$P_{rs} = 2 \sum_{j=1}^{occ.} C_r C_s$	Bond order between atoms r and s.
$Q_r = 2 \sum_{j=1}^{occ.} C_r^2$	Total electron charge density at atom r.
$Q_{rf} = 2\ C_{rf}^2$	Frontier charge density at atom r.

$$\mathcal{E}_r = 2 \sum_{j=1}^{m} C_{rj}^2 E_j$$

Atom energy of atom r.
(in occupied levels)

$$\mathcal{E}_r^+ = E_r - C_{rf}^2 E_f$$

Electrophilic atom stabilization energy.
(E_f=frontier eigenvalue)

$$\mathcal{E}_r^- = E_r + C_{rf}^2 E_f$$

Nucleophilic atom stabilization energy.

$$\Pi_{rr} = 4 \sum_{j=1} \sum_{k=m+1} \frac{C_{rj}^2 \times C_{rk}^2}{E_k - E_j}$$

Atom self-polarizability.

II. Molecule and Ion Code Numbers, Atom Numbering System

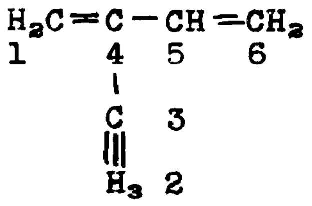
A. Propylene (PROP).

$$\underset{1}{H_3}\equiv\underset{2}{C}-\underset{3}{CH}-\underset{4}{CH_2}$$

B. Butadiene (BUT, BUTN).

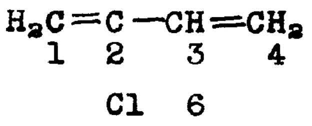
$$\underset{1}{H_2C}=\underset{2}{CH}-\underset{3}{CH}-\underset{4}{CH_2}$$

C. Isoprene (ISOP).



$$\underset{1}{H_2C}=\underset{4}{C}-\underset{5}{CH}=\underset{6}{CH_2};\quad \underset{4}{C}-\underset{3}{C}\equiv\underset{2}{H_3}$$

D. Chloroprene (CLOR).



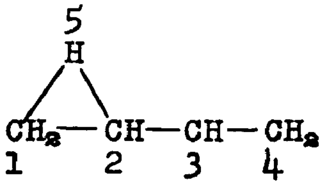
$$\underset{1}{H_2C}=\underset{2}{C}-\underset{3}{CH}=\underset{4}{CH_2};\quad \underset{6}{Cl}$$

E. Protonated Butadiene

1. Hyperconjugative (HBUT)

$H_3\equiv C-CH-CH-CH_2$
1 2 3 4 5

2. Pi Complex (PICOM)

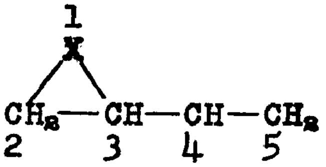


F. Halogenated Butadiene

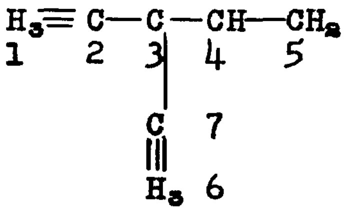
1. Linear (LINX).

$X-CH_2-CH-CH-CH_2$
1 2 3 4 5

2. Halonium Ion (HALON)

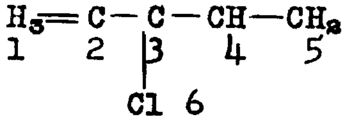


G. Protonated Isoprene (HISOP)



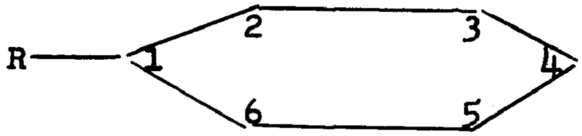
$H_3\equiv C-\underset{\underset{H_3}{\overset{|||}{C}}}{C}-CH-CH_2$

H. Protonated Chloroprene (HCLOR)

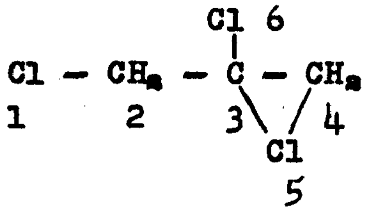


$H_3= C-\underset{Cl}{\overset{}{C}}-CH-CH_2$

I. Substituted Benzene (BENZ)



J.



III. Tables of Input and Computed Values

Table A-1

Propylene Integrals and Bond Orders

H_{11}	H_{22}	H_{33}	H_{44}	H_{12}	H_{23}	H_{34}	P_{12}	P_{23}	P_{34}
-.5	-.1	0	0	2.5	0.7	1.0	.966	.1985	.9799

Table A-2

Propylene C_r, q_{rf}, $\mathcal{E}_r^+$, $\mathcal{E}_r$

E#	C_1	C_2	C_3	C_4		1	2	3	4
E_3	.2055	-.0395	-.6844	.6984	Q_{rf}	.1148	.0375	.8563	.9913
E_2	.2396	.1370	-.6543	-.7040	$\mathcal{E}_r^+$	1.9311	2.4556	.7210	.5192
E_1	.6322	.7204	.2623	.1117	$\mathcal{E}_r$	1.9845	2.4730	1.1189	.9799

Table B-1

Butadiene Integrals and Bond Orders, Perturbations

BUT#	H_{11}	H_{22}	H_{33}	H_{44}	H_{12}	H_{23}	H_{34}	P_{12}	P_{23}	P_{34}
BUT1	0	0	0	0	1.0	1.0	1.0	.8952	.4476	.8952
HBUTN1	0	0	0	0	.1	1.0	1.3	.8137	.5812	.8137
HBUTN2	-.5	0	0	0	.1	1.0	1.3	.2569	.6016	.7983

Table B-2

Butadiene and Perturbations C_r, Q_{rf}, $\mathcal{E}_r^+$, $\mathcal{E}_r^-$, $\mathcal{E}_r$

BUT#	E#	C_1	C_2	C_3	C_4		1	2	3	4
BUT1	E_2	.6015	.3720	-.3720	-.6015	Q_{rf}	.7238	.2764	.2764	.7238
	E_1	.3720	.6015	.6015	.3720	$\mathcal{E}_r^+$	.6714	1.2559	1.2559	.6714
						$\mathcal{E}_r$	.8952	1.3414	1.3414	.8952
HBUTN1	E_3	.7066	-.5597	-.0263	.4321	Q_{rf}	.9986	.6266	.0014	.3734
	E_2	.7066	.5597	-.0263	-.4321	$\mathcal{E}_r^-$	.0417	.6378	1.6391	1.0430
	E_1	.0263	.4321	.7066	.5597	$\mathcal{E}_r$	.0023	.6130	1.6390	1.0282
HBUTN2	E_3	.9873	-.1135	-.0407	.1033	Q_{rf}	.0468	1.2270	.0001	.7262
	E_2	.1529	.7833	-.0057	-.6026	$\mathcal{E}_r^-$	.0017	.6197	1.6394	1.0333
	E_1	.0202	.4319	.7068	.5599	$\mathcal{E}_r$	.0014	.6122	1.6394	1.0288

Table C-1

Isoprene Integrals and Bond Orders

H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{66}	H_{14}	H_{45}	H_{56}	H_{23}	H_{34}	P_{14}	P_{45}	P_{56}	P_{23}	P_{34}
0	-.5	-.1	0	0	0	1.0	1.0	1.0	2.5	.7	.8797	.4382	.8969	.9792	.1841

Table C-2

Isoprene Cr, Q_{rf}, $\mathcal{E}_r^+$, $\mathcal{E}_r$

E#	C_1	C_2	C_3	C_4	C_5	C_6		1	2	3	4	5	6
E_3	.6147	-.1188	-.0525	.3714	-.3535	-.5851	Q_{rf}	.7557	.0282	.0055	.2795	.2500	.6846
E_2	.3314	-.2912	-.2343	.5008	.5895	.3901	$\mathcal{E}_r^+$	.6514	1.0919	2.4676	1.3633	1.2596	.6901
E_1	.1380	.5989	.6932	.3302	.1671	..0698	$\mathcal{E}_r$	.8797	1.9904	2.4692	1.4467	1.3351	.8969

Table D-1

Chloroprene Integrals and Bond Orders

H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{25}	P_{12}	P_{23}	P_{34}	P_{25}
0	.3	0	0	1.8	1	1	1	.6	.8763	.4366	.8975	.1835

Table D-2

Chloroprene C_r, Q_{rf}, $\mathcal{E}_r^+$, $\mathcal{E}_r$

E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
E_3	.5919	.3654	-.3646	-.5906	-.1854	Q_{rf}	.7006	.2671	.2659	.6976	.0688
E_2	.2671	.3805	.5262	.3693	-.6087	$\mathcal{E}_r^+$	.6600	1.6667	1.2520	.6822	3.6207
E_1	.2334	.5152	.2937	.1331	.7591	$\mathcal{E}_r$	.8763	1.7491	1.3341	.8975	3.6419

Table E-1

Linear Protonated Butadiene Integrals and Bond Orders

HBUT#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}	P_{12}	P_{23}	P_{34}	P_{45}
HBUT2	-.5	-.1	-.02	0	0	1	1	1	1	.6635	.6806	.5262	.8360
HBUT3	-.5	-.1	0	0	0	.5	.5	.5	.5	.5275	.7632	.4931	.8630
HBUT4	-.5	-.1	0	0	0	1	1	1	1	.6602	.6829	.5276	.8348
HBUT5	-.5	-.1	0	0	0	2	2	2	2	.7277	.6322	.5508	.8141
HBUT6	-.5	-.1	0	0	0	3	2	1	1	.8369	.5316	.5540	.7985
HBUT7	-.5	-1.0	0	0	0	3	3	1	1	.7054	.6892	.4395	.8597
HBUT8	-.5	-.1	0	0	0	2	3	1	1	.5540	.8199	.3569	.9071
HBUT9	-.5	-1.0	0	0	0	3	2	1.5	1	.8615	.4791	.6987	.6582
HBUT10	-.5	-1.0	0	0	0	3	3	1.5	1	.7471	.6364	.5881	.7370
HBUT11	-.5	-.1	0	0	0	2	3	1.5	1	.6042	.7589	.4977	.8132
HBUT12	-.5	-.1	0	0	0	2.5	.7	.7	1	.9550	.2803	.5392	.8361
HBUT13	-.5	-.1	0	0	0	1	.7	.7	1	.7361	.6311	.4561	.8826
HBUT14	-.5	-.1	0	0	0	2.5	.7	.5	1	.9506	.2977	.4158	.9060
HBUT15	-.5	-.1	0	0	0	3	2	1.5	1	.8672	.4752	.7028	.6537
HBUT16	-.5	-.1	0	0	0	3	3	1.5	1	.7538	.6339	.5930	.7318
HBUT17	-.5	-.1	0	0	0	3	3	1	1	.7128	.6871	.4440	.8565

Table E-1 (Cont.)

HBUT#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}	P_{12}	P_{23}	P_{34}	P_{45}
HBUT19	-.5	-.1	0	0	0	3	1	.5	1	.9369	.3413	.4029	.9102
HBUT20	-.5	-.1	0	0	0	3	1	1	.5	.9599	.2664	.8509	.4825
HBUT21	-.5	-.1	0	0	0	3	.5	1	1	.9851	.1538	.6947	.7150
HBUT22	-.5	-.1	0	0	0	3	.5	1	.5	.9880	.1363	.8832	.4563
HBUT23	0	0	0	0	0	2.5	.7	.7	1	.9694	.2862	.7267	.8285
HBUT24	-.2	0	0	0	0	2.5	.7	.7	1	.9645	.2566	.5464	.8313
HBUT25	-.5	0	0	0	0	2.5	.7	.7	1	.9538	.2790	.5395	.8360
HBUT26	-.8	0	0	0	0	2.5	.7	.7	1	.9391	.3028	.5324	.8406
HBUT27	-.2	-.1	0	0	0	2.5	.7	.7	1	.9649	.2570	.5463	.8314
HBUT28	-.8	-.1	0	0	0	2.5	.7	.7	1	.9409	.3052	.5319	.8409
HBUT29	-.5	-.3	0	0	0	2.5	.7	.7	1	.9563	.2827	.5386	.8365
HBUT30	-.5	-.5	0	0	0	2.5	.7	.7	1	.9560	.2848	.5380	.8368
HBUT31	0	-.1	0	0	0	2.5	.7	.7	1	.9691	.2427	.5510	.8284
HBUT32	0	-.3	0	0	0	2.5	.7	.7	1	.9492	.2422	.5509	.8282
HBUT33	0	0	0	-.2	0	2.5	.7	.7	1	.9692	.2427	.5491	.8254
HBUT34	0	0	-.2	0	0	2.5	.7	.7	1	.9718	.2330	.4971	.8630
HBUT35	0	0	.2	0	0	2.5	.7	.7	1	.9668	.2509	.6104	.7824

Table E-1 (Cont.)

HBUT#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}	P_{12}	P_{23}	P_{34}	P_{45}
HBUT36	0	0	0	.2	0	2.5	.7	.7	1	.9692	.2427	.5491	.8254
HBUT37	0	0	0	-0	-.2	2.5	.7	.7	1	.9704	.2384	.6099	.7818
HBUT38	0	0	0	0	.2	2.5	.7	.7	1	.9679	.2472	.4879	.8665
HBUT39	-.5	-.1	0	0	0	2.5	.5	1	1	.9784	.1837	.6902	.7182
HBUT40	-.5	-.1	0	0	0	2.5	.7	1	1	.9616	.2533	.6749	.7281
HBUT41	-.5	-.1	0	0	0	2.5	1	1	1	.9284	.3507	.6448	.7471
HBUT42	-.5	-.1	0	0	0	2.5	.7	1	.5	.9706	.2204	.8651	.4724
HBUT43	-.5	-.1	0	0	0	2.5	.7	1	.7	.9667	.2344	.7870	.5988
HBUT44	1	1	1	1	1	2.5	.7	.7	1	.9683	.2425	.5494	.8283
HBUT45	-.5	-.1	0	0	0	3	1	1	1	.9497	.2979	.6602	.7364
HBUT46	-.5	-.1	0	0	0	2.5	.7	1	1/.7	.9563	.2730	.5457	.8333
HBUT47	-.5	-.1	0	0	0	2.5	.7	.5	.5/.7	.9537	.2865	.5321	.8395
HBUT48	-.5	-.1	-.02	0	0	2.5	.7	.7	1	.9554	.2792	.5338	.8398
HBUT49	.5	.1	.02	0	0	2.5	.7	.7	1	.9739	.2132	.5675	.8162
HBUT50	-.5	-.1	-.02	0	0	1	.7	.7	1	.7402	.6269	.4537	.8841
HBUT51	.5	.1	.02	0	0	1	.7	.7	1	.9111	.3798	.5452	.8190

Table E-1 (Cont.)

HBUT#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}	P_{12}	P_{23}	P_{34}	P_{45}
HBUT52	-.5	-.1	0	0	0	5	1.4	1	1	.9650	.2561	.6691	.7288
HBUT53	-.5	-.1	0	0	0	5	1.4	.7	1	.9610	.2717	.5347	.8365
HBUT54	.5	-.1	0	0	0	.5	.5	.5	.5	.8189	.3710	.6920	.6538
HBUT55	.5	-.1	0	0	0	1	1	1	1	.8581	.4611	.6387	.7220

Table E-2

Linear Protonated Butadiene C_r, Q_{rf}, $\mathcal{E}_r^-$, $\mathcal{E}_r$

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT2	E_3	.5508	.1822	-.5634	-.0981	.5800	Q_{rf}	.6067	.0664	.6348	.0193	.6728
	E_2	.4184	.5710	.1324	-.4538	-.5248	$\mathcal{E}_r^-$	.3943	1.2329	1.1385	1.3605	.7791
	E_1	.2067	.4491	.5893	.5484	.3279	$\mathcal{E}_r$	.4457	1.2385	1.1922	1.3622	.8360
HBUT3	E_3	.4896	.3394	-.5258	-.1781	.5805	Q_{rf}	.4794	.2304	.5530	.0634	.6739
	E_2	.3381	.5949	.2328	-.4180	-.5503	$\mathcal{E}_r^-$	.0890	.5238	.5858	.6732	.3798
	E_1	.1539	.4071	.5973	.5757	.3499	$\mathcal{E}_r$	.1258	.5415	.6282	.6780	.4315
HBUT4	E_3	.5516	.1860	-.5633	-.0942	.5787	Q_{rf}	.6086	.0692	.6347	.0178	.6697
	E_2	.4173	.5696	.1324	-.4551	-.5261	$\mathcal{E}_r^-$	.3941	1.2323	1.1588	1.3609	.7802

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT4	E_1	.2059	.4488	.5927	.5467	.3255	$\mathcal{E}_r$	.4437	1.2379	1.2105	1.3623	..8348
HBUT5	E_3	.5706	.0954	-.5738	-.0479	.5777	Qrf	.6513	.0182	.6584	.0046	.6676
	E_2	.4597	.5419	.0706	-.4763	-.5129	$\mathcal{E}_r^-$	1.1312	2.6146	2.3114	2.7295	1.5729
	E_1	.2424	.4732	.5871	.5264	.3091	$\mathcal{E}_r$	1.1852	2.6161	2.3659	2.7298	1.6282
HBUT6	E_3	.4237	.0578	-.6352	-.0581	.6405	Qrf	.3590	.0067	.8071	.0067	.8205
	E_2	.2752	.1598	-.3055	-.6991	-.5628	$\mathcal{E}_r^-$	2.1345	3.4699	1.5807	1.3522	.7613
	E_1	.5331	.7024	.4479	.1416	.0410	$\mathcal{E}_r$	2.1508	3.4702	1.6173	1.3525	.7985
HBUT7	E_3	.5797	.0641	-.5620	-.0975	.5784	Qrf	.6721	.0082	.6316	.0190	.6691
	E_2	.2972	.1624	-.1814	-.6939	-.6091	$\mathcal{E}_r^-$	1.7556	3.2708	2.4539	1.2976	.8033
	E_1	.4644	.6556	.5705	.1645	.0440	$\mathcal{E}_r$	1.8123	3.2715	2.5071	1.2992	.8597
HBUT8	E_3	.7031	.0847	-.4732	-.1314	.5073	Qrf	.9886	.0143	.4479	.0346	.5146
	E_2	.2515	.1972	-.0909	-.6886	-.6446	$\mathcal{E}_r^-$	.8057	3.4406	2.7345	1.2595	.8394
	E_1	.3330	.6829	.6207	.1867	.0518	$\mathcal{E}_r$	.9338	3.4425	2.7925	1.2640	.9071
HBUT9	E_3	.3595	.0524	-.5147	-.0485	.7751	Qrf	.2585	.0055	.5298	.0047	1.2015
	E_2	.4268	.2726	-.3109	-.6570	-.4639	$\mathcal{E}_r^-$	2.1362	2.6277	1.9896	1.7061	.6206
	E_1	.5080	.6189	.5239	.2769	.0878	$\mathcal{E}_r$	2.1443	2.6278	2.0061	1.7062	.6582

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT10	E_3	.4926	.0624	-.4743	-.0867	.7218	Q_{rf}	.4852	.0078	.4499	.0150	1.0421
	E_2	.4061	.2409	-.2230	-.6720	-.5252	ε_r^-	1.8573	3.2334	2.7643	1.6183	.6744
	E_1	.4359	.6326	.5879	.2453	.0636	ε_r	1.8864	3.2339	2.7913	1.6912	.7370
HBUT11	E_3	.6179	.0926	-.4150	-.1298	.6485	Q_{rf}	.7635	.0172	.3445	.0337	.8411
	E_2	.3515	.2880	-.1154	-.6637	-.5828	ε_r^-	.9137	3.3815	2.9888	1.5564	.7290
	E_1	.3076	.6530	.6321	.2725	.0727	ε_r	.9902	3.3833	3.0233	1.5597	.8132
HBUT12	E_3	.2245	.0426	-.7973	-.0140	.5585	Q_{rf}	.1008	.0036	1.2714	.0004	.6238
	E_2	.1518	.1027	-.3527	-.7027	-.5901	ε_r^-	1.9563	2.4767	.5577	1.2136	.8283
	E_1	.6379	.7241	.2435	.0893	.0382	ε_r	1.9563	2.4767	.5736	1.2136	.8361
HBUT13	E_3	.4832	.1824	-.6962	-.0606	..4948	Q_{rf}	.4671	.0666	.9694	.0073	.4896
	E_2	.4587	.6191	.1847	-.3950	-.4649	ε_r^-	.4516	1.0660	.7016	1.2014	.8526
	E_1	.2132	.3940	.5106	.5894	.4372	ε_r	.4802	1.0701	.7610	1.2019	.8826
HBUT14	E_3	.2438	.0459	-.8662	-.0129	.4335	Q_{rf}	.1189	.0042	1.5007	.0003	.3758
	E_2	.1112	.0713	-.2747	-.7053	-.6400	ε_r^-	1.9496	2.4780	.4141	1.1139	.9004
	E_1	.6425	.7275	.2315	.0609	.0261	ε_r	1.9514	2.4781	.4163	1.1139	.9060

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT15	E_3	.3458	.0507	-.5178	-.0469	.7795	Q_{rf}	.2392	.0051	.5361	.0044	1.2151
	E_2	.3687	.2429	-.3618	-.6797	-.4606	$\mathcal{E}_r^-$	2.2028	3.4476	1.9885	1.7078	.6171
	E_1	.5057	.6804	.4784	.2206	.0624	$\mathcal{E}_r$	2.2100	3.4477	2.0047	1.7079	.6537
HBUT16	E_3	.4786	.0611	-.4790	-.0850	.7284	Q_{rf}	.4582	.0074	.4588	.0145	1.0611
	E_2	.3721	.2268	-.2641	-.6875	-.5174	$\mathcal{E}_r^-$	1.9111	4.0599	2.7646	1.6205	.6698
	E_1	.4301	.6800	.5542	.2075	.0489	$\mathcal{E}_r$	1.9379	4.0604	2.7913	1.6213	.7318
HBUT17	E_3	.5672	.0634	-.5686	-.0964	.5845	Q_{rf}	.6435	.0080	.6466	.0186	.6833
	E_2	.2748	.1522	-.2108	-.7015	-.6040	$\mathcal{E}_r^-$	1.8068	4.0969	2.4520	1.2989	.8002
	E_1	.4506	.6981	.5381	.1377	.0332	$\mathcal{E}_r$	1.8598	4.0976	2.5053	1.3005	.8564
HBUT19	E_3	.2861	.0438	-.8557	-.0175	.4286	Q_{rf}	.1637	.0038	1.4645	.0006	.3674
	E_2	.1130	.0602	-.2667	-.7065	-.6429	$\mathcal{E}_r^-$	2.3874	3.0464	.5127	1.1116	.9027
	E_1	.6380	.7235	.2580	.0504	.0174	$\mathcal{E}_r$	2.3908	3.0464	.5427	1.1116	.9102
HBUT20	E_3	.1480	.0241	-.4419	-.0193	.8842	Q_{rf}	.0438	.0012	.3906	.0007	1.5637
	E_2	.2334	.1198	-.5638	-.7057	-.3395	$\mathcal{E}_r^-$	2.4286	3.0403	1.1151	1.0922	.2327
	E_1	.6296	.7197	.2796	.0986	.0169	$\mathcal{E}_r$	2.4289	3.0403	1.1173	1.0922	.2413

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT21	E_3	.1176	.0193	-.7020	-.0048	.7021	Q_{rf}	.0277	.0007	.9857	.0000	.9858
	E_2	.1165	.0736	-.4787	-.7049	-.5050	ε_r^-	2.4969	2.9259	.7682	1.4096	.7115
	E_1	.6670	.7257	.1546	.0643	.0233	ε_r	2.4970	2.9259	.7716	1.4096	.7150
HBUT22	E_3	.0747	.0124	-.4459	-.0050	.8919	Q_{rf}	.0112	.0003	.3977	.0001	1.5908
	E_2	.1297	.0690	-.6130	-.7063	-.3222	ε_r^-	2.5012	2.9257	.9508	1.1114	.2260
	E_1	.6678	.7263	.1520	.0569	.0103	ε_r	2.5012	2.9257	.9513	1.1114	.2282
HBUT23	E_3	.2236	.0000	-.7985	-.0000	.5589	Q_{rf}	.1000	.0000	1.2752	.0000	.6248
	E_2	.1355	.0652	-.3721	-.7041	-.5858	ε_r^-	2.4231	2.5930	.5555	1.2138	.8282
	E_1	.6758	.7041	.2067	.0652	.0250	ε_r	2.4231	2.5930	.5555	1.2138	.8282
HBUT24	E_3	.2235	.0170	-.7984	-.0056	.5589	Q_{rf}	.0999	.0001	1.2747	.0001	.6247
	E_2	.1398	.0782	-.3656	-.7039	-.5875	ε_r^-	2.2937	2.5908	.5557	1.2138	.8282
	E_1	.6587	.7155	.2192	.0724	.0288	ε_r	2.2299	2.5908	.5621	1.2138	.8313
HBUT25	E_3	.2229	.0424	-.7976	-.0139	.5587	Q_{rf}	.0994	.0036	1.2724	.0004	.6243
	E_2	.1467	.0993	-.3547	-.7033	-.5900	ε_r^-	1.9612	2.5798	.5570	1.2136	.8282
	E_1	.6323	.7312	.2389	.0848	.0355	ε_r	1.9632	2.5798	.5729	1.2136	.8360
HBUT26	E_3	.2219	.0675	-.7963	-.0222	.5583	Q_{rf}	.0985	.0091	1.2681	.0010	.6233

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT26	E_2	.1538	.1222	-.3426	-.7022	-.5924	$\mathcal{E}_r^-$	1.7218	2.5596	.5594	1.2133	.8282
	E_1	.6053	.7447	.2595	.0989	.0435	$\mathcal{E}_r$	1.7238	2.5598	.5846	1.2133	.8406
HBUT27	E_3	.2241	.0170	-.7982	-.0056	.5588	Q_{rf}	.1005	.0006	1.2743	.0001	.6246
	E_2	.1437	.0803	-.3643	-.7036	-.5875	$\mathcal{E}_r^-$	2.2268	2.4905	.5560	1.2138	.8282
	E_1	.6646	.7085	.2227	.0757	.0307	$\mathcal{E}_r$	2.2273	2.4905	.5624	1.2138	.8314
HBUT28	E_3	.2244	.0682	-.7957	-.0225	.5579	Q_{rf}	.1007	.0093	1.2664	.0010	.6225
	E_2	.1604	.1273	-.3395	-.7013	-.5925	$\mathcal{E}_r^-$	1.7132	2.4537	.5605	1.2132	.8284
	E_1	.6103	.7374	.2655	.1050	.0473	$\mathcal{E}_r$	1.7152	2.4539	.5859	1.2132	.8409
HBUT29	E_3	.2278	.0432	-.7966	-.0142	.5580	Q_{rf}	.1038	.0037	1.2693	.0004	.6228
	E_2	.1631	.1102	-.3482	-.7014	-.5900	$\mathcal{E}_r^-$	1.9421	2.2792	.5587	1.2135	.8285
	E_1	.6486	.7095	.2533	.0992	.0444	$\mathcal{E}_r$	1.9434	2.2792	.5749	1.2135	.8365
HBUT30	E_3	.2312	.0438	-.7960	-.0144	.5575	Q_{rf}	.1069	.0038	1.2671	.0004	.6217
	E_2	.1761	.1188	-.3428	-.6996	-.5898	$\mathcal{E}_r^-$	1.9243	2.0933	.5596	1.2134	.8287
	E_1	.6584	.6943	.2637	.1107	.0518	$\mathcal{E}_r$	1.9257	2.0933	.5760	1.2134	.8368
HBUT31	E_3	.2236	-.0000	-.7985	.0000	.5589	Q_{rf}	.1000	.0000	1.2752	.0000	.6248
	E_2	.1386	.0666	-.3712	-.7038	-.5858	$\mathcal{E}_r^-$	2.4227	2.4944	.5555	1.2139	.8282
	E_1	.6819	.6971	.2095	.0677	.0265	$\mathcal{E}_r$	2.4227	2.4944	.5555	1.2139	.8282

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT32	E_3	.2236	.0000	-.7985	.0000	.5589	Q_{rf}	.1000	.0000	1.2752	.0000	.6248
	E_2	.1453	.0698	-.3693	-.7032	-.5857	ε_r^-	2.4191	2.3060	.5552	1.2139	.8282
	E_1	.6937	.6828	.2151	.0733	.0298	ε_r	2.4191	2.3060	.5552	1.2139	.8282
HBUT33	E_3	.2236	.0000	-.7985	.0000	.5589	Q_{rf}	.1000	.0000	1.2752	.0000	.6248
	E_2	.1354	.0600	-.3888	-.6747	.6096	ε_r^-	2.4231	2.5930	.5543	1.0262	.8254
	E_1	.6763	.7045	.2053	.0594	.0228	ε_r	2.4231	2.5930	.5543	1.0262	.8254
HBUT34	E_3	.2224	-.0113	-.7922	-.0715	.5636	Q_{rf}	.0989	.0003	1.2552	.0102	.6354
	E_2	.1198	.5641	-.3330	-.7115	-.6044	ε_r^-	2.4233	2.5926	.3724	1.2103	.8227
	E_1	.6792	.7055	.1918	.0607	.0234	ε_r	2.4296	2.5927	.4520	1.2109	.8630
HBUT35	E_3	.2224	.0113	-.7922	.0715	.5636	Q_{rf}	.0989	.0003	1.2552	.0102	.6354
	E_2	.1546	.0762	-.4178	-.6928	-.5619	ε_r^-	2.4233	2.5926	.7724	1.2103	.8227
	E_1	.6716	.7022	.2240	.0703	.0269	ε_r	2.4170	2.5926	.6928	1.2096	.7824
HBUT36	E_3	.2236	-.0000	-.7985	-.0000	.5589	Q_{rf}	.1000	.0000	1.2752	.0000	.6248
	E_2	.1364	.7123	-.3545	-.7321	-.5610	ε_r^-	2.4231	2.5930	.5543	1.4262	.8254
	E_1	.6750	.7036	.2084	.0721	.0277	ε_r	2.4231	2.5930	.5543	1.4262	.8254
HBUT37	E_3	.2236	-.0556	-.7982	.0764	.5540	Q_{rf}	.1000	.0001	1.2744	.0117	.6139

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT37	E_2	.1427	.0650	-.4039	-.7220	-.5394	ε_r^-	2.4230	2.5929	.5542	1.2084	.6462
	E_1	.6759	.7042	.2065	.0643	.0229	ε_r	2.4261	2.5929	.5938	1.2087	.6653
HBUT38	E_3	.2236	.0056	-.7982	-.0764	.5540	Q_{rf}	.1000	.0001	1.2744	.0117	.6139
	E_2	.1280	.0653	-.3379	-.6814	-.6331	ε_r^-	2.4230	2.5929	.5542	1.2084	1.0462
	E_1	.6756	.7040	.2070	.0662	.0275	ε_r	2.4199	2.5929	.5146	1.2080	1.0271
HBUT39	E_3	.1409	.0276	-.6997	-.0069	.6998	Q_{rf}	.0397	.0015	.9792	.0001	.9794
	E_2	.1664	.1252	-.4605	-.6991	-.5058	ε_r^-	1.9979	2.4303	.7772	1.4083	.7133
	E_1	.6483	.7225	.2070	.1119	.0490	ε_r	1.9981	2.4303	.7821	1.4084	.7182
HBUT40	E_3	.1952	.0376	-.6928	-.0131	.6931	Q_{rf}	.0762	.0028	.9600	.0003	.9607
	E_2	.2125	.1578	-.4305	-.6946	-.5119	ε_r^-	1.9665	2.4741	.8431	1.4029	.7190
	E_1	.6258	.7147	.2723	.1410	.0599	ε_r	1.9672	2.4741	.8522	1.4030	.7281
HBUT41	E_3	.2727	.0505	-.6787	-.0253	.6796	Q_{rf}	.1488	.0051	.9212	.0013	.9237
	E_2	.2591	.1881	-.3819	-.6900	-.5250	ε_r^-	1.9036	2.5652	.9874	1.3919	.7299
	E_1	.5895	.7048	.3507	.1680	.0675	ε_r	1.9063	2.5653	.9955	1.3919	.7471
HBUT42	E_3	.1251	.0246	-.4434	-.0138	.8871	Q_{rf}	.0313	.0012	.3933	.0004	1.5738
	E_2	.2248	.1397	-.5725	-.7011	-.3327	ε_r^-	1.9777	2.4733	1.0178	1.1013	.2301

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT42	E_1	.6310	.7193	.2644	.1178	.0251	$\mathcal{E}_r$	1.9778	2.4733	1.0194	1.1013	.2362
HBUT43	E_3	.1595	.0311	-.5657	-.0146	.8083	Q_{rf}	.0509	.0019	.6399	.0004	1.3068
	E_2	.2170	.1441	-.5156	-.6989	-.4217	$\mathcal{E}_r^-$	1.9730	2.4736	.9471	1.2062	.4109
	E_1	.6296	.7181	.2667	.1244	.0370	$\mathcal{E}_r$	1.9734	2.4736	.9511	1.2062	.4191
HBUT44	E_3	.2236	-.0000	-.7985	-.0000	.5589	Q_{rf}	.1000	.0000	1.2752	.0000	.6248
	E_2	.1355	.0652	-.3721	-.7041	-.5858	$\mathcal{E}_r^-$	3.4231	3.5930	1.5555	2.2138	1.8282
	E_1	.6758	.7041	.2067	.0615	.0250	$\mathcal{E}_r$	3.3731	3.5930	.9179	2.2138	1.5158
HBUT45	E_3	.2300	.0363	-.6873	-.0182	.6878	Q_{rf}	.1058	.0026	.9448	.0007	.9461
	E_2	.2026	.1249	-.4268	-.7010	-.5194	$\mathcal{E}_r^-$	2.4126	3.0411	.9456	1.3965	.7239
	E_1	.6276	.7162	.2824	.1094	.0374	$\mathcal{E}_r$	2.4140	3.0412	.9581	1.3965	.7364
HBUT46	E_3	.2246	.0427	-.7974	-.0098	.5584	Q_{rf}	.1009	.0036	1.2718	.0002	.6236
	E_2	.2365	.2064	-.3193	-.6815	-.5788	$\mathcal{E}_r^-$	1.9593	2.4748	.7208	1.7361	1.1825
	E_1	.6118	.7017	.2884	.1916	.1156	$\mathcal{E}_r$	1.9605	2.4749	.7368	1.7361	1.1904
HBUT47	E_3	.2245	.0426	-.7971	-.0196	.5586	Q_{rf}	.1008	.0036	1.2707	.0008	.6242
	E_2	.1264	.0684	-.3586	-.7069	-.5925	$\mathcal{E}_r^-$	1.9535	2.4779	.4506	.8657	.5918
	E_1	.6431	.7280	.2304	.0546	.0167	$\mathcal{E}_r$	1.9547	2.4779	.4666	.8657	.5996

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT48	E_3	.2242	.0414	-.7971	-.0211	.5588	Q_{rf}	.1005	.0034	1.2707	.0009	.6244
	E_2	.1499	.1012	-.3489	-.7036	-.5920	ε_r^-	1.9564	2.4768	.5379	1.2134	.8280
	E_1	.6384	.7244	.2415	.0886	.0379	ε_r	1.9583	2.4768	.5619	1.2135	.8398
HBUT49	E_3	.2242	-.0414	-.7971	.0211	.5588	Q_{rf}	.1005	.0034	1.2707	.0009	.6244
	E_2	.1255	.0358	-.3913	-.7030	-.5793	ε_r^-	2.9564	2.6783	.5779	1.2134	.8280
	E_1	.7099	.6797	.1774	.0487	.0168	ε_r	2.9545	2.6767	.5538	1.2134	.8162
HBUT50	E_3	.4820	.1772	-.6968	-.0656	.4964	Q_{rf}	.4647	.0629	.9710	.0086	.4928
	E_2	.4606	.6214	.1844	-.3925	-.4623	ε_r^-	.4518	1.0667	.6806	1.2012	.8515
	E_1	.2133	.3932	.5057	.5916	.4405	ε_r	.4825	1.0709	.7448	1.2017	.8841
HBUT51	E_3	.4820	-.1773	-.6968	.0656	.4964	Q_{rf}	.4647	.0629	.9710	.0086	.4928
	E_2	.4359	.2748	-.2181	-.6208	-.5491	ε_r^-	1.4518	1.2667	.7206	1.2011	.8515
	E_1	.5657	.5936	.4209	.3259	.2104	ε_r	1.4211	1.2626	.6565	1.2006	.8190
HBUT52	E_3	.1944	.0187	-.6933	-.0131	.6935	Q_{rf}	.0756	.0007	.9613	.0003	.9620
	E_2	.1446	.0542	-.4592	-.7076	-.5144	ε_r^-	4.3657	5.0798	1.0186	1.3979	.7197
	E_1	.6614	.7176	.2132	.0451	.0092	ε_r	4.3664	5.0798	1.0277	1.3979	.7288

Table E-2 (Cont.)

HBUT#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HBUT53	E_3	.2238	.0213	-.7980	-.0140	.5590	Qrf	1.0014	.0009	1.2737	.0004	.6249
	E_2	.1132	.0384	-.3685	-.7079	-.5906	$\mathcal{E}_r^-$	4.3516	5.0819	.7388	1.2108	.8287
	E_1	.6628	.7184	.2088	.0310	.0063	$\mathcal{E}_r$	4.3529	5.0819	.7547	1.2108	.8365
HBUT54	E_3	.4238	-.3118	-.5686	.1616	.6113	Qrf	.3593	.1945	.6466	.0522	.7474
	E_2	.5760	.1750	-.3129	-.5829	-.4471	$\mathcal{E}_r^-$	1.1229	.5484	.5742	.6764	.3763
	E_1	.5983	.5159	.4657	.3514	.1887	$\mathcal{E}_r$	1.0992	.5356	.5315	.6729	.3269
HBUT55	E_3	.5288	-.1819	-.5754	.0921	.5897	Qrf	.5592	.0661	.6621	.0169	.6956
	E_2	.5941	.3758	-.1308	-.5240	-.4627	$\mathcal{E}_r^-$	1.4174	1.2441	1.1515	1.3621	.7763
	E_1	.4033	.5102	.5482	.4575	.2592	$\mathcal{E}_r$	1.3738	1.2389	1.0998	1.3608	.7220

Table E-3

Pi Complex Integrals

H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{15}	H_{25}	H_{12}	H_{23}	H_{34}
-.2	-.2	0	0	-.2	2	2	2	.7	1

Table E-4

Pi Complex Cr, Q_{rf}, $\bar{\mathcal{E}_r}$, $\mathcal{E}_r$

E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
E3	.1465	−.1976	−.6401	.7130	.1465	Q_{rf}	.0429	.0781	.8194	1.0167	.0429
E_2	−.1103	.0429	.7052	.6903	−.1103	$\mathcal{E}_r$	2.4954	2.5752	.7475	.5240	2.4956
E_1	.5689	.5821	.1136	.0295	.5689	$\bar{\mathcal{E}_r}$	2.5247	2.6102	1.1153	.9803	2.5149

Table F-1

Linear Halobutadiene Complex Integrals

LINX#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}
LINX1	1.8	.3	0	0	0	.6	1	.7	1
LINX2	1.0	.2	0	0	0	.5	1	.7	1

Table F-2

Linear Halobutadiene Complex Cr, Q_{rf}, $\mathcal{E}_r^-$, $\mathcal{E}_r$

LINX#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
LINX1	E_3	.2996	–.5490	–.3995	.3845	.5490	Q_{rf}	.1795	.6028	.3193	.2957	.6028
	E_2	.3659	–.2753	–.5082	–.5859	–.4344	$\mathcal{E}_r^-$	3.5746	1.1617	1.0418	1.0734	.7302
	E_1	.8678	.4223	.2361	.1024	.0490	$\mathcal{E}_r$	3.5117	.9506	.9300	.9699	.5192
LINX2	E_3	.5440	–.4532	–.4458	.2760	.4730	Q_{rf}	.5918	.4109	.3974	.1523	.4475
	E_2	.6669	.1676	–.1783	–.5262	–.4674	$\mathcal{E}_r^-$	1.8838	1.1305	1.0332	1.1330	.8094
	E_1	.4743	.5480	.5177	.3840	.2434	$\mathcal{E}_r$	1.7112	1.0106	.9173	1.0885	.6788

Table F-3

Halonium Ion Integrals

HALON#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{13}	H_{23}	H_{34}	H_{45}
HALON1	1	.2	.2	0	0	.5	.5	.8	.7	1
HALON2	1	.1	.1	0	0	.5	.5	.8	.7	1
HALON3	.5	.1	.1	0	0	.5	.5	.8	.7	1
HALON4	1	.2	.2	0	0	.6	.6	.8	.7	1
HALON5	1	.2	.2	0	0	.5	.5	1	.7	1

Table F-4

Halonium Ion C_r, Q_{rf}, $\mathcal{E}_r^-$, $\mathcal{E}_r$

HALON#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HALON1	E_3	.6479	-.5144	-.4438	.0868	.3333	Q_{rf}	.8395	.5293	.3940	.0151	.2222
	E_2	-.4479	-.1610	.1068	.6352	.5989	$\mathcal{E}_r^-$	1.8992	.8886	1.1577	1.1864	.8890
	E_1	.6123	.4584	.5453	.3006	.1652	$\mathcal{E}_r$	1.7898	.8196	1.1064	1.1844	.8601
HALON2	E_3	.6259	-.5204	-.4647	.0726	.3408	Q_{rf}	.7836	.5416	.4320	.0105	.2323
	E_2	-.4521	-.1521	.1006	.6343	.6001	$\mathcal{E}_r^-$	1.9262	.8006	1.0615	1.1868	.8929
	E_1	.6312	.4427	.5299	.3077	.1738	$\mathcal{E}_r$	1.8428	.7429	1.0156	1.1856	.8681
HALON3	E_3	.7651	-.4022	-.4118	-.0092	.2886	Q_{rf}	1.1706	.3235	.3392	.0002	.1665
	E_2	-.4296	-.3192	-.0733	.5818	.6080	$\mathcal{E}_r^-$	1.0390	.8774	1.1087	1.1861	.9101
	E_1	.4664	.4607	.5837	.4076	.2517	$\mathcal{E}_r$	1.0577	.8825	1.1141	1.1861	.9127
HALON4	E_3	.6613	-.4975	-.4557	.0439	.3249	Q_{rf}	.8747	.4950	.4153	.0039	.2111
	E_2	-.3854	-.1589	.1174	.6569	.6171	$\mathcal{E}_r^-$	1.9549	.9310	1.1839	1.1886	.8963
	E_1	.6372	.4657	.5381	.2632	.1353	$\mathcal{E}_r$	1.8958	.8975	1.1558	1.1883	.8820
HALON5	E_3	.6872	-.4841	-.4144	.1141	.3296	Q_{rf}	.9445	.4687	.3435	.0261	.2173
	E_2	-.4404	-.1446	.0967	.6391	.6061	$\mathcal{E}_r^-$	1.8435	1.0714	1.3229	1.1737	.8954
	E_1	.5744	.4956	.5682	.2827	.1468	$\mathcal{E}_r$	1.6800	.9903	1.2635	1.1692	.8577

Table G-1

Protonated Isoprene Integrals*

HISOP#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{23}	H_{34}	H_{45}
HISOP1	-.5	-.1	0	0	0	2.5	.7	1	1
HISOP2	-.5	-.1	0	0	0	.5	.5	.5	.5
HISOP3	-.5	-.1	0	0	0	1	1	1	1
HISOP4	0	0	0	0	0	2.5	.7	.7	1
HISOP5	-.5	-.1	0	0	0	2.5	.7	.7	1

Table G-2

Protonated Isoprene C_r, Q_{rf}, ε_r^-, ε_r

HISOP#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HISOP1	E_4	.1911	.0354	-.6792	-.0248	.6801	Q_{rf}	.0730	.0025	.9226	.0012	.9251
	E_3	-.1824	-.1325	.3835	.6901	.5245	ε_r^-	1.9689	2.4729	.9732	1.3923	.7295
	E_2	.4796	.5196	.0000	.0000	.0000	ε_r	1.9703	2.4729	.9900	1.3924	.7464
	E_1	.4177	.4985	.3484	.1674	.0674						

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*Parameters for atoms 6 and 7 are identical in value with those for atoms 1 and 2 respectively.

Table G-2 (Cont.)

HISOP#	E#	C_1	C_2	C_3	C_4	C_5		1	2	3	4	5
HISOP2	E_4	-.3991	-.2234	.4528	.2473	-.5617	Q_{rf}	.3186	.0998	.4100	.1223	.6310
	E_3	-.3964	-.5855	.0000	.0000	.0000	ε_r^-	.0992	.5062	.7548	.6475	.3808
	E_2	.1833	.3392	.1730	-.5313	-.6248	ε_r	.1342	.5172	.7999	.6610	.4503
	E_1	.1276	.3682	.6407	.4723	.2504						
HISOP3	E_4	.4719	.1219	-.4892	-.1256	.5195	Q_{rf}	.4454	.0297	.4786	.0315	.5398
	E_3	.4483	.5468	-.0000	.0000	.0000	ε_r^-	.4292	1.2009	1.4998	1.3249	.8132
	E_2	.2284	.3231	.0994	-.5553	-.6072	ε_r	.4830	1.2045	1.5576	1.3287	.8785
	E_1	.1593	.3881	.6306	.4445	.2296						
HISOP4	E_4	.2182	-.0000	-.7793	-.0000	.5455	Q_{rf}	.0952	.0000	1.2145	.0000	.5951
	E_3	-.1245	-.0591	.3446	.7022	.5918	ε_r^-	2.4263	2.5915	.7017	1.2076	.8363
	E_2	.5000	.5000	.0000	.0000	.0000	ε_r	2.4263	2.5915	.7017	1.2076	.8363
	E_1	.4590	.4965	.2787	.0836	.0309						
HISOP5	E_4	.2184	.0395	-.7770	-.0260	.5451	Q_{rf}	.0954	.0031	1.2073	.0014	.5943
	E_3	-.1328	-.0886	.3136	.7008	.5996	ε_r^-	1.9596	2.4753	.7054	1.2070	.8360
	E_2	.4796	.5196	.0000	.0000	.0000	ε_r	1.9619	2.4754	.7343	1.2070	.8502
	E_1	.4291	.5075	.3204	.1095	.0446						

Table H-1

Protonated Chloroprene Integrals

HCLOR#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{66}	H_{12}	H_{23}	H_{34}	H_{45}	H_{36}
HCLOR1	-.5	-.1	.3	0	0	1.8	2.5	.7	.7	1	.6
HCLOR2	-.5	-.1	.2	0	0	1	2.5	.7	.7	1	.5

Table H-2

Protonated Chloroprene C_r, Q_{rf}, ε_r^-, ε_r

E#	C_1	C_2	C_3	C_4	C_5	C_6		1	2	3	4	5	6
<u>HCLOR1</u>													
E_3	-.1243	-.0827	.2949	.6838	.5883	-.2775	Q_{rf}	.0309	.0137	.1740	.9352	.6923	.1540
E_2	.3224	.3167	-.2216	-.1074	-.0549	-.8556	ε_r^-	1.9395	2.4661	.8978	.6622	.4267	3.5197
E_1	.5595	.6534	.3535	.1233	.0510	.3424	ε_r	1.9575	2.4741	.9989	1.2057	.8290	3.6092
<u>HCLOR2</u>													
E_3	-.0000	-.0000	.0000	-.5025	-.5025	.7035	Q_{rf}	.0000	.0000	.0000	.5051	.5051	.9899
E_2	-.2236	-.1674	.4466	.4862	.3544	.6004	ε_r^-	1.9633	2.4749	.9401	.9522	.6063	1.5369
E_1	.6213	.7120	.2882	.1039	.0439	.1056	ε_r	1.9633	2.4749	.9401	1.2047	.8588	2.0318

Table I-1

BENZ#	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{66}	H_{12}	H_{23}	H_{34}	H_{45}	H_{56}	H_{61}
BENZ1	.3	.1	0	0	0	.1	1.5	1.1	1	1	1.1	1.5
BENZ2	-.3	-.1	0	0	0	-.1	.75	.9	1	1	.9	.75

Table I-2

Substituted Benzene C_r, Q_{rf}, $\mathcal{E}_r^+$, $\mathcal{E}_r$

E#	C_1	C_2	C_3	C_4	C_5	C_6		1	2	3	4	5	6
BENZ1													
E_3	-.0000	-.5112	-.4885	-.0000	.4885	.5112	Q_{rf}	.0000	.5227	.4773	.0000	.4773	.5227
E_2	-.4076	-.1297	.4197	.6692	.4197	-.1297	$\mathcal{E}_r^+$	2.3387	1.5238	1.1137	1.3494	1.1137	1.5238
E_1	.6020	.4719	.2736	.2064	.2736	.4719	$\mathcal{E}_r$	2.3387	1.8246	1.3884	1.3494	1.3884	1.8246
BENZ2													
E_3	-.6214	-.4073	.1634	.4782	.1634	-.4073	Q_{rf}	.7723	.3318	.0534	.4573	.0534	.3318
E_2	-.0000	.4859	.5137	.0000	-.5137	-.4859	$\mathcal{E}_r^+$	.4602	.8848	1.2499	1.1701	1.2499	.8848
E_1	.2364	.3242	.4719	.5372	.4719	.3242	$\mathcal{E}_r$	.7240	.9981	1.2681	1.3264	1.2681	.9981

Table J-1

Dichloroproprne Halonium Ion Integrals

H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{66}	H_{12}	H_{23}	H_{34}	H_{45}	H_{35}	H_{36}
1.8	.3	.4	.3	1.8	1.8	.6	.6	.7	.4	.4	.6

Table J-2

Dichloropropene Halonium Ion C_r, Q_{rf}, ε_r^-, ε_r

E#	C_1	C_2	C_3	C_4	C_5	C_6		1	2	3	4	5	6
E_3	-.0766	-.0062	.0606	-.1392	-.6451	.7449	Q_{rf}	.0117	.0001	.0073	.0388	.8322	1.1099
E_2	.8963	.2984	-.0510	-.0852	-.2727	-.1532	ε_r^-	3.5064	.5591	.9696	.4069	2.5756	2.4472
E_1	.2475	.2097	.4542	.2722	.5717	.5362	ε_r	3.5173	.5591	.9764	.4427	3.3449	3.4731

Table K-1

SCF Propylene Computations

	Atom or Bond Number					Atom Number			
	1	2	3	4		1	2	3	4
H_{rr}	-.5	-.1	0	0	Q_{fr}	.6005	.5936	.1565	.6494
H_{rs}	1.0014	.8016	1.0096		Q_r	.7603	1.1661	.9886	1.0850
C_{r2}	.5479	.5448	-.2797	-.5698		.2204	.7963	1.1604	.6050
C_{r1}	.2827	.5350	.6450	.4667		.5206	1.0931	1.2386	.9297

Table K-2

SCF Butadiene Computations

	Atom or Bond Number					Atom or Bond Number			
	1	2	3	4		1	2	3	4
H_{rr}	0	0	0	0	Q_{fr}	.6828	.3172	.3172	.6828
H_{rs}	1.0128	.7956	1.0128		Q_r	1.0000	1.0000	1.0000	1.0000
C_{r2}	.5843	.3983	-.3983	-.5843	P_{rs}	.9308	.3656	.9398	
C_{r1}	.3983	.5843	.5843	.3983	$\mathcal{E}_r^+$	.7070	1.1240	1.1240	.7070
E_1, E_2, E_3, E_4	1.4859	.6903	-.6903	-1.4859	$\mathcal{E}_r$	.9427	1.2335	1.2335	.9427

Table K-3

SCF Isoprene Computations

Atom or Bond Number (1-4, 2-3, 3-4, 4-5, 5-6)

	1	2	3	4	5	6		1	2	3	4	5	6
H_{rr}	0	0	0	0	0	0	Q_{fr}	.7407	.4939	.4359	.1626	.0321	.1547
H_{rs}	.9884	1.0042	.7923	.7851	1.0160		Q_r	1.0795	.7648	1.1679	.9901	1.0010	.9967
C_{r3}	.6086	-.4868	-.4669	.2851	-.1268	-.2781	P_{rs}	.8663	.9069	.3612	.3408	.9382	

Table K-3 (Cont.)

	1	2	3	4	5	6		1	2	3	4	5	6
C_{r2}	.1811	.3381	.4708	.1646	-.5148	-.5823	$\mathcal{E}_r^+$	.6851	.4186	.9792	1.3725	1.2133	.9174
C_{r1}	.3696	.1764	.3799	.6218	.4684	.2862	$\mathcal{E}_r$	.8566	.5284	1.0802	1.4102	1.2208	.9532
E	1.6630	.8982	.4631	-.6644	-1.1843	-1.7756							

Table K-4

SCF Protonated Butadiene $\mathcal{E}_r^-$, Q_{fr} for Changing H_{12}/H_{23}

Atom Number

H_{12}/H_{23}		1	2	3	4	5
2.0/.7	$\mathcal{E}_r^-$	1.6649	2.2242	.8093	1.2909	.7009
2.5/.7	$\mathcal{E}_r^-$	2.1445	2.6717	.7849	1.2959	.6863
3.0/.7	$\mathcal{E}_r^-$	2.6200	3.1259	.7676	1.3192	.6777
2.0/.7	Q_{fr}	.1217	.0055	.9802	.0009	.8917
2.5/.7	Q_{fr}	.0785	.0025	.9906	.0004	.9280
3.0/.7	Q_{fr}	.0546	.00013	.9951	.0002	.9487

Table L

Selected Protonated Butadiene Eigenvalues

HBUT#	E_1	E_2	E_3	E_4	E_5
12	2.3378	1.1910	-.0251	-1.2106	-2.8931
29	2.2350	1.1887	-.0255	-1.2108	-2.9874
30	2.1365	1.1861	-.0259	-1.2110	-3.0857
37	2.6048	1.1386	-.0621	-1.2763	-2.6050
38	2.6050	1.2763	.0621	-1.1386	-2.6048
23	2.6049	1.2019	-.0000	-1.2019	-2.6049
31	2.5558	1.2015	-.0000	-1.2024	-2.6549

IV. Sample Program

The following pages illustrate the type of symbolically coded program used for the computations involved in this thesis. Explanatory notes accompany the various machine instructions and sequences.

The IBM 704 is an electronic digital computer using a stored program. A machine word contains 36 binary bits. 24 binary words may be punched on one IBM card, while the magnetic core storage can contain over 32,000 of these words.

The machine has been constructed to "understand" a symbolic language somewhat more compact than instructions coded directly in binary. The Share Assembly Program, therefore, allows us to transfer our mathematical instructions to the machine in the form of 3 letter operation codes. The machine converts these operations into binary form for computation.

Members of the Share organization, which includes educational institutions and industrial concerns using the 704, frequently contribute to the subrouting library any sequences of instructions they have coded and which might be of future use to others. The following illustrative program uses four of these subroutines, two from the library tape and two from the card library.

Two series of computations are illustrated for an iterative treatment of protonated butadiene. The input resonance integrals differ in each series. The method here used for obtaining the atomic orbital coefficients is to define certain factors (F1, F2, F3, F4) which are simply related to quantities in the secular determinant. Thus,

$$F1=(E-H11)/H12$$

$$F2=F1(E-H22)/H23-H_{12}/H_{23}$$

$$F_3=F_2(E-H_{33})/H_{34}-F_1(H_{23}/H_{34})$$

$$F_4=F_3(H_{45})/(E-H_{55})$$

From the normalization condition and the fact that

$$C_2=C_1(F_1)$$

$$C_3=C_1(F_2)$$

$$C_4=C_1(F_3)$$

$$C_5=C_1(F_4)$$

the coefficients are evaluated for as many energy levels as desired.

```
RUN N377-307-JORDAN        INITIATES AUTOMATIC OPERATOR PROGRAM.
BIN CNTRC*00               MATRIX  CONTRACTION SUBROUTINE
BIN HDIAG*00               MATRIX  DIAGONILIZATION SUBROUTINE
CST             COMBINE SYMBOL TABLES
SAP N377-HBUT-SCF                     SHARE ASSEMBLY PROGRAM
```

```
                                  PRG OFF          LIST SYMBOLIC PROGRAM, INDICATING IN OCTAL NOTATION
                                  SMT OFF      ALL STORAGE ASSIGNMENTS AND INSTRUCTIONS.  ALSO  PUNCH
                    01750         ORG 1000     BINARY DECK OF CARDS FOR FUTURE.  SAVES COMPILING TIME.
01750  0 14000 0 01751   START   TOV *+1      ORIGIN OF PROGRAM IS DECIMAL LOCATION 1000.  OVERFLOW AND
01751  0 76000 0 00012           DCT          DIVIDE-CHECK INDICATORS TURNED OFF.  THIS ALLOWS LIBRARY
01752  0 76100 0 00000           NOP          SUBROUTINE CLOUD1 (OCTAL      ) TO OPERATE  EFFECTIVELY.
01753  0 16100 0 01754           TQO *+1      TURN OFF MQ OVERFLOW INDICATOR AND LIGHT.
01754  0 60000 0 02476           STZ CTIT     STORE ZERO IN SYMBOLIC LOCATION CTIT.  THIS WILL COUNT
01755  0 60000 0 02500           STZ TOUGH    NO. OF ITERATIONS.  STORE ZERO IN TOUGH.
01756  0 07400 4 00156  CONTRL  TSX CNTRC,4       SUBROUTINE CALLING SEQUENCE IS SPECIFIED IN
01757  0 02475 0 02501           PZE TRI,0,RCN  SHARE WRITEUP 248.  TRI IS INITIAL ADDRESS OF  MATRIX IN
01760  0 00000 0 02537           PZE H        TRIANGULAR FORM.  H IS INITIAL ADDRESS OF SQUARE MATRIX.
01761  0 07400 4 00226           TSX HDIAG,4  THIS IS NORMAL RETURN OF CNTRC AND START OF HDIAG CALLING
01762  0 02475 0 02501           PZE TRI,0,RCN  SEQUENCE.  HDIAG USES JACOBI METHOD OF SOLVING  FOR EIGEN
01763 -0 00000 0 00000           MZE          VALUES.  EIGENVECTORS CALCULATED LATER.  RCN IS ADDRESS
01764  0 00000 0 00000           HTR 0        CONTAINING SIZE OF THE MATRIX, IN THIS CASE A 5TH ORDER
01765  0 00000 0 00000           HTR 0        DETERMINANT.   HTR INDICATES HALT AND TRANSFER TO ERROR
01766  0 60100 0 02477           STO R        STOP ROUTINE BUILT INTO HDIAG.
01767  0 50000 0 02476           CLA CTIT          COUNTING OF ITERATIONS STARTS HERE.  CTIT NOW CON-
01770  0 30000 0 02410           FAD I        TAINS ZERO.  ASMOV CALLS IN CLOUD1 AFTER EACH  ADDITION
01771  0 07400 4 02415           TSX ASMOV,4  AND MULTIPLICATION.  CTIT NOW CONTAINS DECIMAL 1.  IN
01772  0 60100 0 02476           STO CTIT     FLOATING POINT FORM.  TRI, NOW THE INITIAL ADDRESS
01773  0 50000 0 02501           CLA TRI      CONTAINING THE EIGENVALUES, IS STORED IN E.  THIS PROCED-
01774  0 60100 0 02532           STO E        URE PLACES THE ENERGY VALUES IN MORE CONVENIENT CONSEC-
01775  0 50000 0 02503           CLA TRI+2    UTIVE LOCATIONS FOR THE NEXT PROCEDURE, STARTING AT LOOP,
01776  0 60100 0 02533           STO E+1      WHICH SORTS THEM IN ORDER OF DECREASING MAGNITUDE.
01777  0 50000 0 02506           CLA TRI+5         COLUMNS 1-6 OF A CARD CONTAIN ADDRESS OF INSTRUCTION
02000  0 60100 0 02534           STO E+2      AS FOR EXAMPLE CONTRL.  COLUMNS 7 AND 11 ARE ALWAYS BLANK
02001  0 50000 0 02512           CLA TRI+9    WHILE COLUMNS 8-10 CONTAIN THE THREE LETTER OPERATION
02002  0 60100 0 02535           STO E+3      CODE.  STARTING IN COLUMN 12 WE HAVE THE ADDRESS, TAG,
02003  0 50000 0 02517           CLA TRI+14   AND DECREMENT, WITH NO INTERVENING BLANKS.
02004  0 60100 0 02536           STO E+4
02005  0 53400 3 02461           LXA COUNT,3       THIS ROUTINE, (LOOP-1 THROUGH NEXT+1), MAKES USE OF
02006  0 50000 2 02537    LOOP   CLA E+5,2    INDEXING AND ADDRESS MODIFICATION, A VERY VALUABLE
02007  0 56000 1 02537           LDQ E+5,1    CHARACTERISTIC BUILT INTO THE IBM 704 WHICH CANNOT BE
02010  0 04000 0 02013           TLQ SKIP     DESCRIBED IN DETAIL HERE.  IT ALLOWS ONE TO  PERFORM
```

```
02011 -0 60000 2 02537        STQ E+5,2
02012  0 60100 1 02537        STO E+5,1
02013  1 77777 2 02014   SKIP TXI NEXT,2,-1
02014  3 00000 2 02006   NEXT TXH LOOP,2,0
02015  2 00001 3 02006        TIX LOOP,3,1
02016  0 53400 1 02473        LXA SIGMA,1
02017  0 50000 1 02537 REPEAT CLA E+5,1
02020  0 30200 0 02537        FSB H
02021  0 07400 4 02415        TSX ASMOV,4
02022  0 24100 0 02540        FDP H+1
02023  0 07400 4 02433        TSX DIVOV,4
02024 -0 60000 1 02577        STQ F1+3,1
02025  0 50000 0 02540        CLA H+1
02026  0 24100 0 02546        FDP H+7
02027  0 07400 4 02433        TSX DIVOV,4
02030 -0 60000 0 00012        STQ COMMON
02031  0 50000 1 02537        CLA E+5,1
02032  0 30200 0 02545        FSB H+6
02033  0 07400 4 02415        TSX ASMOV,4
02034  0 24100 0 02546        FDP H+7
02035  0 07400 4 02433        TSX DIVOV,4
02036  0 26000 1 02577        FMP F1+3,1
02037  0 07400 4 02415        TSX ASMOV,4
02040  0 30200 0 00012        FSB COMMON
02041  0 07400 4 02415        TSX ASMOV,4
02042  0 60100 1 02602        STO F2+3,1
02043  0 50000 0 02546        CLA H+7
02044  0 24100 0 02554        FDP H+13
02045  0 07400 4 02433        TSX DIVOV,4
02046  0 26000 1 02577        FMP F1+3,1
02047  0 07400 4 02415        TSX ASMOV,4
02050  0 60100 0 00012        STO COMMON
02051  0 50000 1 02537        CLA E+5,1
02052  0 30200 0 02553        FSB H+12
02053  0 07400 4 02415        TSX ASMOV,4
02054  0 24100 0 02554        FDP H+13
```

SEQUENCES OF CONTROLLED LOGICAL INSTRUCTIONS, AND TO MAKE VARIOUS TYPES OF DECISIONS. EIGENVALUES ARE FIRST SORTED, THEN STORED IN DECREASING ORDER (MOST POSITIVE VALUE LAST).

WITH REPEAT WE INITIATE A SEQUENCE OF INSTRUCTIONS DESIGNED TO CALCULATE FROM THE NEWLY COMPUTED EIGENVALUES THE A.O. COEFFICIENTS, FROM WHICH THE VARIOUS REACTIVITY PARAMETERS, INCLUDING THE FRONTIER ELECTRON CHARGE DENSITIES, (FECD1-FECD5), ATOM ENERGIES (AE) AND ATOM STABILIZATION ENERGIES (ASE) ARE LATER OBTAINED.

LOGICAL CONTROL EXISTS OVER THIS SEQUENCE IN THAT WE REQUIRE 3 SETS OF VALUES FOR THE A. O. COEFFICIENTS, ONE FOR EACH OF THE OCCUPIED LEVELS, AND ONE FOR THE FRONTIER LEVEL. THUS AT COEFF WE HAVE COMPUTED FIRST THE FRONTIER COEFFICIENTS. CONTROL IS THEN RETURNED TO REPEAT AND THE TWO REMAINING SETS ARE COMPUTED AND STORED CONSECUTIVELY. COEFF IS HERE DEFINED FOR ILLUSTRATIVE PURPOSES ONLY. IT IS NECESSARY TO DEFINE SYMBOLICALLY ONLY THOSE LOCATIONS WHICH ONE MUST SPECIFICALLY REFER TO IN HIS PROGRAM, E.G. LOOP, SKIP, NEXT, REPEAT, CONTRL, ETC. IN THIS SEQUENCE FREQUENT USE IS MADE OF INDEX REGISTER 1, REFERRED TO IN THE TAGGED INSTRUCTIONS. PRIOR TO ENTERING THIS ROUTINE THIS INDEX REGISTER IS LOADED WITH THE ADDRESS OF THREE, NAMELY THE INTEGER 3. (LXA THREE,1) COEFF REFERS TO A TIX INSTRUCTION WHICH DECREMENTS THIS TO 2 AFTER THE FIRST SET OF COEFFICIENTS HAS BEEN COMPUTED AND CHANGES CONTROL BACK TO REPEAT. WHEN INDEX REGISTER 1 CONTAINS 1, JUST PRIOR TO THE THIRD PASS THROUGH REPEAT, AND CONTROL REACHES COEFF AFTER THIS PASS, THE TIX MAKES THE DECISION THAT THIS IS ENOUGH FOR NOW AND IT WILL ALLOW CONTROL TO GO TO THE FOLLOWING INSTRUCTION, STZ ORDER.

```
02055   0 07400 4 02433        TSX DIVOV,4
02056   0 26000 1 02602        FMP F2+3,1
02057   0 07400 4 02415        TSX ASMOV,4
02060   0 30200 0 00012        FSB COMMON
02061   0 07400 4 02415        TSX ASMOV,4
02062   0 60100 1 02605        STO F3+3,1
02063   0 50000 1 02537        CLA E+5,1
02064   0 30200 0 02567        FSB H+24
02065   0 07400 4 02415        TSX ASMOV,4
02066   0 60100 0 00012        STO COMMON
02067   0 50000 0 02562        CLA H+19
02070   0 24100 0 00012        FDP COMMON
02071   0 07400 4 02433        TSX DIVOV,4
02072   0 26000 1 02605        FMP F3+3,1
02073   0 07400 4 02415        TSX ASMOV,4
02074   0 60100 1 02610        STO F4+3,1
02075   0 56000 1 02610        LDQ F4+3,1
02076   0 26000 1 02610        FMP F4+3,1
02077   0 07400 4 02415        TSX ASMOV,4
02100   0 60100 0 00012        STO COMMON
02101   0 56000 1 02605        LDQ F3+3,1

02102   0 26000 1 02605        FMP F3+3,1
02103   0 07400 4 02415        TSX ASMOV,4
02104   0 30000 0 00012        FAD COMMON
02105   0 07400 4 02415        TSX ASMOV,4
02106   0 60100 0 00012        STO COMMON
02107   0 56000 1 02602        LDQ F2+3,1
02110   0 26000 1 02602        FMP F2+3,1
02111   0 07400 4 02415        TSX ASMOV,4
02112   0 30000 0 00012        FAD COMMON
02113   0 07400 4 02415        TSX ASMOV,4
02114   0 60100 0 00012        STO COMMON
02115   0 56000 1 02577        LDQ F1+3,1
02116   0 26000 1 02577        FMP F1+3,1
02117   0 07400 4 02415        TSX ASMOV,4
```

NOTICE MANY SYMBOLS ARE DEFINED NEAR THE END OF THE PROGRAM, WHERE THEY WILL NOT INTERRUPT ANY PART OF THE MAIN PROGRAM. SYMBOLS MAY BE DEFINED ONLY ONCE. SHOULD A SYMBOL BE ACCIDENTALLY MULTIPLY DEFINED, THE COMPUTER WOULD NOT COMPILE THIS SYMBOLIC PROGRAM INTO BINARY FORM IN ITS ENTIRETY AND WOULD PRINT AN M AT THE FAR LEFT OF THIS LISTING. THE SHARE ASSEMBLER STATISTICS WOULD TAG THE PROGRAM AND SYMBOLS AS BAD. THE COMPUTER POSSESSES MANY SUCH ERROR-DETECTION DEVICES WHICH ARE QUITE USEFUL WHEN PROGRAMS ARE BEING COMPILED AND RUN FOR THE FIRST TIME.

TWO PARTS OF THE MACHINE ARE THE ARITHMETIC ELEMENT AND THE CONTROL ELEMENT. THE ARITHMETIC ELEMENT CONSISTS OF THE ACCUMULATOR (AC) AND THE MULTIPLIER-QUOTIENT REGISTER (MQ), ONE OF WHICH IS ALWAYS INVOLVED IN ANY ARITHMETIC OPERATION. ADDITION AND DIVISION REQUIRE THE ACCUMULATOR BE LOADED FROM STORAGE LOCATION INVOLVED. FOR EXAMPLE, CLA H+19 IS AN INSTRUCTION WHICH TAKES THE CONTENTS OF STORAGE LOCATION H+19 (WITHOUT DISTURBING IT) AND CONVEYS IT TO THE AC. THE NEXT INSTRUCTION, FDP COMMON, USES THIS VALUE IN THE AC AS THE DIVIDEND TO EXECUTE A DIVISION BY THE CONTENTS OF SYMBOLIC LOCATION COMMON. MULTIPLICATION REQUIRES THAT THE MQ BE LOADED (LDQ) WITH THE MULTIPLIER PRIOR TO THE EXECUTION OF THE MULTIPLICATION (FMP).

ANOTHER IMPORTANT PART OF CENTRAL PROCESSING UNIT IS THE CONTROL ELEMENT, WHICH CONSISTS MAINLY OF THE INDEX REGISTERS AND THE INSTRUCTION LOCATION COUNTER. THESE PROVIDE FOR THE SYSTEM OF INDEXING AND ADDRESS MODIFICATION MENTIONED ABOVE AND FOR A NORMAL, SKIP, OR TRANSFER TYPE INSTRUCTION.

NOTICE THE FREQUENT USE OF TSX ASMOV,4 AND TSX DIVOV 4. THE FORMER IS USED IN ADDITION, SUBTRACTION, AND MUL-

```
02120  0 30000 0 00012        FAD COMMON      TIPLICATION, WHILE THE LATTER IS USED IN DIVISION TO AID
02121  0 07400 4 02415        TSX ASMOV,4     IN DETECTING ERRORS IN BOTH PROGRAMMING AND COMPUTING.
02122  0 30000 0 02410        FAD I           SUCH ERRORS ARE FREQUENT ENOUGH TO REQUIRE CAREFUL
02123  0 07400 4 02415        TSX ASMOV,4     ATTENTION ON THE PART OF THE PROGRAMMER TO BUILDING INTO
02124  0 60100 0 00012        STO COMMON      HIS PROGRAM A SERIES OF CHECKS.  ASMOV AND DIVOV
02125  0 50000 0 02412        CLA ONE         REFER TO SEQUENCES OF INSTRUCTIONS IN LIBRARY  SUBROUTINE
02126  0 24100 0 00012        FDP COMMON      CLOUD1, WHICH IS ON MAGNETIC TAPE IN BINARY FORM AND IS
02127  0 07400 4 02433        TSX DIVOV,4     BROUGHT THROUGH THE CENTRAL PROCESSING UNIT INTO MAGNETIC
02130 -0 60000 0 00012        STQ COMMON      CORE STORAGE FOR PROGRAM USAGE.  SEVERAL TYPES OF ERRORS
                                              ARE ACCOUNTED FOR AND ON SUCH AN OCCASION COMPUTATION IS
                                              HALTED AND A PRINT OUT IS MADE OF THE CONTENTS OF THE
                                              ARITHMETIC AND CONTROL ELEMENTS AS WELL AS A  SIGNIFICANT
                                              PORTION OF CORE STORAGE IF DESIRED, SO THAT A  THOROUGH
                                              DIAGNOSIS MAY BE MADE OF WHAT WENT WRONG AND WHERE IN THE
                                              SEQUENCE OF OPERATIONS IT OCCURED.
02131  0 50000 0 00012        CLA COMMON
02132  0 07400 4 01137        TSX SQRT,4      HERE IS A LIBRARY SUBROUTINE FOR OBTAINING SQUARE ROOTS,
02133  0 00000 0 00000        HTR             WITH NEXT AN ERROR STOP IN CASE OF IMAGINARY ROOTS, THEN
02134  0 60100 1 02613        STO C1+3,1      THE NORMAL RETURN WITH THE ROOT IN THE AC TO BE STORED IN
02135  0 56000 1 02613        LDQ C1+3,1      C1, C1+1, AND C1+2 IN THE SUCCESSIVE PASSES   THROUGH THE
02136  0 26000 1 02577        FMP F1+3,1      REPEAT-COEFF ROUTINE.  NOTICE THAT EACH SUBROUTINE
02137  0 07400 4 02415        TSX ASMOV,4     CALLING SEQUENCE USES INDEX REGISTER 4.  F1-F5 HAVE BEEN
02140  0 60100 1 02616        STO C2+3,1      USED IN COMPUTING C1, USING THE NORMALIZATION CONDITION,
02141  0 56000 1 02613        LDQ C1+3,1      AND THE OTHER A.O. COEFFICIENTS ARE RELATED AND
02142  0 26000 1 02602        FMP F2+3,1      CALCULATED IN THIS ROUTINE AS SHOWN IN MORE DETAIL
02143  0 07400 4 02415        TSX ASMOV,4     ELSEWHERE IN THE APPENDIX.
02144  0 60100 1 02621        STO C3+3,1           THE NEXT SERIES, STARTING WITH BOND, CALCULATES BOND
02145  0 56000 1 02613        LDQ C1+3,1      ORDERS.  NOTICE THE SEQUENCE OF INSTRUCTIONS FOR EACH
02146  0 26000 1 02605        FMP F3+3,1      LOOP.  INDEX REGISTER 1 STARTS WITH THE VALUE OF SIGMA,
02147  0 07400 4 02415        TSX ASMOV,4     NAMELY 3, AND IT IS CHANGED TO 1 AS CONTROL REACHES THE
02150  0 60100 1 02624        STO C4+3,1      TIX INSTRUCTION.  WHEN THE INTEGER IN THE INDEX REGISTER
02151  0 56000 1 02613        LDQ C1+3,1      REACHES THE VALUE OF THE DECREMENT OF THE TIX INSTRUCTION
02152  0 26000 1 02610        FMP F4+3,1      THE TRANSFER IS NO LONGER EXECUTED, AND THE INSTRUCTION
02153  0 07400 4 02415        TSX ASMOV,4     LOCATION COUNTER CONTAINS THE ADDRESS OF THE FOLLOWING
02154  0 60100 1 02627        STO C5+3,1      INSTRUCTION WHICH IS THEN EXECUTED.
02155  2 00001 1 02017  COEFF TIX REPEAT,1,1  (THIS IS THE INSTRUCTION THAT TRANSFERS TO REPEAT.)
```

```
02156  0 60000 0 02627         STZ ORDER
02157  0 60000 0 02630         STZ ORDER+1
02160  0 60000 0 02631         STZ ORDER+2
02161  0 60000 0 02632         STZ ORDER+3
02162  0 53400 1 02473         LXA SIGMA,1      LOAD INDEX REGISTER 1 WITH THE ADDRESS OF SIGMA.
02163  0 56000 1 02613    BOND LDQ C1+3,1       LOAD MQ WITH C1+1, C1+2 WHEN C(IR1) IS 2, 1.
02164  0 26000 1 02616         FMP C2+3,1       MULTIPLY C(MQ) BY C(C2+1,C2+2) IN TURN.
02165  0 07400 4 02415         TSX ASMOV,4      ERROR DETECTION FOR AC OVERFLOW, ETC.
02166  0 30000 0 02627         FAD ORDER        ADD CONTENTS OF SYMBOLIC STORAGE LOCATION ORDER.
02167  0 60100 0 02627         STO ORDER        STORE THE RESULT IN ORDER.  (MULTIPLY BY 2 LATER)
02170  2 00001 1 02163         TIX BOND,1,1     DECREMENT IR1 BY 1 AND TRANSFER CONTROL TO BOND  (FIRST).
02171  0 53400 1 02473         LXA SIGMA,1      C(X) IS SHORTHAND FOR CONTENTS OF X.
02172  0 56000 1 02616     BON LDQ C2+3,1
02173  0 26000 1 02621         FMP C3+3,1            THE NUMBERS ON THE LEFT OF PRINTED LISTING REFER TO
02174  0 07400 4 02415         TSX ASMOV,4      THE ADDRESS OF THIS INSTRUCTION, THE INSTRUCTION  ITSELF,
02175  0 30000 0 02630         FAD ORDER+1      THE DECREMENT (IF ANY), THE TAG (IF ANY) AND THE ADDRESS
02176  0 07400 4 02415         TSX ASMOV,4      OF THE INSTRUCTION TO WHICH THIS INSTRUCTION  REFERS.
02177  0 60100 0 02630         STO ORDER+1      THESE NUMBERS ARE IN OCTAL NOTATION, SINCE BINARY
02200  2 00001 1 02172         TIX BON,1,1      NOTATION IS SPACE-CONSUMING AND LESS READILY READ.
02201  0 53400 1 02473         LXA SIGMA,1      FOR EXAMPLE, THE PREVIOUS INSTRUCTION, TIX BON,1,1 IN
02202  0 56000 1 02621      BN LDQ C3+3,1       OCTAL IS         2 00001 1              REFERS TO TIX
02203  0 26000 1 02624         FMP C4+3,1       ADDRESS, 2000 REFERS TO MACHINE INTERPRETATION OF TIX,
02204  0 07400 4 02415         TSX ASMOV,4      01 REFERS TO THE DECREMENT, THE FIGURE SUBTRACTED
02205  0 30000 0 02631         FAD ORDER+2      FROM C(IR1) BEFORE EXECUTION OF INSTRUCTION.  1 REFERS TO
02206  0 07400 4 02415         TSX ASMOV,4      THE TAG, OR INDEX REGISTER, WHILE       REFERS TO THE
02207  0 60100 0 02631         STO ORDER+2      LOCATION OF TRANSFER, THAT IS, THE OCTAL LOCATION OF BON.
02210  2 00001 1 02202         TIX BN,1,1
02211  0 53400 1 02473         LXA SIGMA,1           THE SEQUENCE OF 5 INSTRUCTIONS STARTING WITH ORD
02212  0 56000 1 02624      BD LDQ C4+3,1       MULTIPLIES THE ABOVE PRODUCTS OF A.O. COEFFICIENTS BY 2.
02213  0 26000 1 02627         FMP C5+3,1       THE 8 INSTRUCTIONS ASSOCIATED WITH BETA USE THE ASSUMED
02214  0 07400 4 02415         TSX ASMOV,4      LINEAR RELATIONSHIP BETWEEN BOND ORDER AND RESONANCE
02215  0 30000 0 02632         FAD ORDER+3      INTEGRAL TO COMPUTE VALUES OF THE LATTER AND STORE THEM
02216  0 07400 4 02415         TSX ASMOV,4      IN NEW THROUGH NEW+3.  THE BOND ORDERS WERE EVALUATED IN
02217  0 60100 0 02632         STO ORDER+3      THE PREVIOUS BLOCK OF INSTRUCTIONS.
02220  2 00001 1 02212         TIX BD,1,1
02221  0 53400 1 02462         LXA SIZE,1
```

```
02222  0 56000 1 02633    ORD LDQ ORDER+4,1
02223  0 26000 0 02411        FMP TWOP
02224  0 07400 4 02415        TSX ASMOV,4
02225  0 60100 1 02633        STO ORDER+4,1
02226  2 00001 1 02222        TIX ORD,1,1
02227  0 53400 1 02462        LXA SIZE,1
02230  0 56000 1 02633   BETA LDQ ORDER+4,1
02231  0 26000 0 02413        FMP M
02232  0 07400 4 02415        TSX ASMOV,4
02233  0 30000 0 02414        FAD B
02234  0 07400 4 02415        TSX ASMOV,4
02235  0 60100 1 02574        STO NEW+4,1
02236  2 00001 1 02230        TIX BETA,1,1          TEST BEGINS A SERIES OF 20 INSTRUCTIONS   DESIGNED
02237  0 50000 0 02571   TEST CLA NEW+1        TO ESTABLISH THE CRITERION FOR SELF-CONSISTENCY.  EACH
02240  0 30200 0 02546        FSB H+7          RESONANCE INTEGRAL, NEWLY EVALUATED FROM THE BETA SERIES,
02241  0 07400 4 02415        TSX ASMOV,4      IS COMPARED, WITH THE EXCEPTION OF H12, WITH THE VALUES
02242  0 76000 0 00003        SSP              USED IN THE MOST RECENT DIAGONALIZATION.  IF AN INTEGRAL
02243  0 30200 0 02460        FSB DELTA        DOES NOT AGREE WITHIN 0.0001 IN THIS COMPARISON, CONTROL
02244  0 07400 4 02415        TSX ASMOV,4      IS TRANSFERRED TO CHANGE, WHERE THE NEWLY COMPUTED BETAS
02245  0 12000 0 02367        TPL CHANGE       ARE PLACED IN THE RESPECTIVE STORAGE LOCATIONS USED FOR
02246  0 50000 0 02572        CLA NEW+2        THE INPUT OF THE MATRIX CONTRACTION SUBROUTINE.
02247  0 30200 0 02554        FSB H+13         IF AGREEMENT IS COMPLETE FOR ALL BETAS, A NORMAL SEQUENCE
02250  0 07400 4 02415        TSX ASMOV,4      IS MAINTAINED THROUGH THE ROUTINE STARTING WITH SQUARE.
02251  0 76000 0 00003        SSP
02252  0 30200 0 02460        FSB DELTA             LET US BRIEFLY FOLLOW THE SYMBOLIC CODING USED IN
02253  0 07400 4 02415        TSX ASMOV,4      THIS TEST SERIES.  SEVEN INSTRUCTIONS ARE USED  PER TEST.
02254  0 12000 0 02367        TPL CHANGE
02255  0 50000 0 02573        CLA NEW+3        IF H23 AND H34 WERE O.K., THE NEW H45 IS PUT IN THE AC.
02256  0 30200 0 02562        FSB H+19         SUBTRACT THE PREVIOUS VALUE OF H45.
02257  0 07400 4 02415        TSX ASMOV,4      ERROR DETECTION SUBROUTINE.
02260  0 76000 0 00003        SSP              SET SIGN POSITIVE OF THIS SUBTRACTION RESULT.
02261  0 30200 0 02460        FSB DELTA        SUBTRACT 0.0001.
02262  0 12000 0 02367        TPL CHANGE       TRANSFER TO SYMBOLIC LOCATION CHANGE IF RESULTS POSITIVE.
02263  0 53400 1 02472        LXA THREE,1      IF RESULT IS ZERO OR NEGATIVE EXECUTE THIS INSTRUCTION.
02264  0 56000 1 02613 SQUARE LDQ C1+3,1            IN THE 21 INSTRUCTIONS STARTING WITH SQUARE EACH AO
02265  0 26000 1 02613        FMP C1+3,1       COEFFICIENT FOR EACH EIGENVALUE IS BEING SQUARED AND
```

```
02266  0 07400 4 02415      TSX ASMOV,4
02267  0 60100 1 02636      STO Q1+3,1
02270  0 56000 1 02616      LDQ C2+3,1
02271  0 26000 1 02616      FMP C2+3,1
02272  0 07400 4 02415      TSX ASMOV,4
02273  0 60100 1 02641      STO Q2+3,1
02274  0 56000 1 02621      LDQ C3+3,1
02275  0 26000 1 02621      FMP C3+3,1
02276  0 07400 4 02415      TSX ASMOV,4
02277  0 60100 1 02644      STO Q3+3,1
02300  0 56000 1 02624      LDQ C4+3,1
02301  0 26000 1 02624      FMP C4+3,1
02302  0 07400 4 02415      TSX ASMOV,4
02303  0 60100 1 02647      STO Q4+3,1
02304  0 56000 1 02627      LDQ C5+3,1
02305  0 26000 1 02627      FMP C5+3,1
02306  0 07400 4 02415      TSX ASMOV,4
02307  0 60100 1 02652      STO Q5+3,1
02310  2 00001 1 02264      TIX SQUARE,1,1
02311  0 53400 1 02472      LXA THREE,1
02312  0 56000 1 02537    V LDQ E+5,1
02313  0 26000 1 02636      FMP Q1+3,1
02314  0 07400 4 02415      TSX ASMOV,4
02315  0 60100 1 02655      STO ER+3,1
02316  2 00001 1 02312      TIX V,1,1
02317  0 53400 1 02472      LXA THREE,1
02320  0 56000 1 02537    W LDQ E+5,1
02321  0 26000 1 02641      FMP Q2+3,1
02322  0 07400 4 02415      TSX ASMOV,4
02323  0 60100 1 02660      STO ER+6,1
02324  2 00001 1 02320      TIX W,1,1
02325  0 53400 1 02472      LXA THREE,1
02326  0 56000 1 02537    X LDQ E+5,1
02327  0 26000 1 02644      FMP Q3+3,1
02330  0 07400 4 02415      TSX ASMOV,4
02331  0 60100 1 02663      STO ER+9,1
```

STORED IN Q1-Q5 AND THE FOLLOWING LOCATIONS. NOTE THAT WE REQUIRE THREE LOCATIONS FOR EACH Q AS WE DID FOR THE C AND F VALUES. WE DEFINE Q1, THEN, AS A BLOCK OF THREE STORAGE REGISTERS STARTING IN LOCATION   OCTAL. WHENEVER WE NEED ONLY ONE REGISTER IN STORAGE THE PZE OR PLUS ZERO INSTRUCTION IS USED. BSS 1 WORKS ALSO.

THE 704 USES TWO TYPES OF ARITHMETIC, FIXED POINT AND FLOATING POINT. WE ARE USING THE LATTER AS CAN BE SEEN BY THE INSTRUCTIONS FAD OR FLOATING ADD, FMP OR FLOATING MULTIPLY, ETC. THIS REQUIRES A SPECIFIC METHOD IN REFERRING TO DATA AND ERROR DETECTION AS WELL AS IN THE FORM OF THE OUTPUT DATA. DETAILS WILL NOT BE DISCUSSED.

HERE THE RESPECTIVE ATOM ENERGIES ARE OBTAINED BY MULTIPLYING ENERGIES BY SQUARES OF COEFFICIENTS, SUMMING THE VALUES FOR THE LOWEST TWO ENERGIES AND MULTIPLYING BY TWO, THE PROCESS BEING COMPLETED IN THE ATSTAB ROUTINE WHERE THE RESULTS WILL BE FOUND IN AE AND THE FOLLOWING 14 STORAGE REGISTERS, EVERY THIRD VALUE BEING THE ATOM ENERGY. IN A LONGER PROGRAM THIS WOULD BE CONSIDERED WASTEFUL OF STORAGE SPACE, BUT THE CODING FOR THIS IS CONVENIENT. ATOM STABILIZATION ENERGIES ARE ALSO COMPUTED AND ARE STORED AT ASE.

WE SHALL DESCRIBE BRIEFLY THE REMAINDER OF A

```
02332  2 00001 1 02326         TIX X,1,1
02333  0 53400 1 02472         LXA THREE,1
02334  0 56000 1 02537       Y LDQ E+5,1
02335  0 26000 1 02647         FMP Q4+3,1
02336  0 07400 4 02415         TSX ASMOV,4
02337  0 60100 1 02666         STO ER+12,1
02340  2 00001 1 02334         TIX Y,1,1
02341  0 53400 1 02472         LXA THREE,1
02342  0 56000 1 02537       Z LDQ E+5,1
02343  0 26000 1 02652         FMP Q5+3,1
02344  0 07400 4 02415         TSX ASMOV,4
02345  0 60100 1 02671         STO ER+15,1
02346  2 00001 1 02342         TIX Z,1,1
02347  0 53400 1 02474         LXA ZIP,1
02350  0 56000 1 02671      VA LDQ ER+15,1
02351  0 26000 0 02411         FMP TWOP
02352  0 60100 1 02710         STO ERT+15,1
02353  2 00001 1 02350         TIX VA,1,1
02354  0 53400 1 02457         LXA FEEN,1
02355  0 50000 1 02712 ATSTAB CLA ERT+17,1
02356  0 30000 1 02711         FAD ERT+16,1
02357  0 60100 1 02727         STO AE+15,1
02360  0 30000 1 02671         FAD ER+15,1
02361  0 60100 1 02744         STO ASE+15,1
02362  2 00003 1 02355         TIX ATSTAB,1,3
02363  077200000201            HLT
02364  076200000221
02365  070000000001
02366  002100000001
02367  0 50000 0 02406 CHANGE CLA TWALF
02370  0 24100 0 02407         FDP SEVEN
02371  0 26000 0 02571         FMP NEW+1
02372  0 60100 0 02540         STO H+1
02373  0 60100 0 02544         STO H+5
02374  0 50000 0 02571         CLA NEW+1
02375  0 60100 0 02546         STO H+7
```

COMPLETE DECK OF IBM CARDS FOR USE IN THE AUTOMATIC OPERATOR PROGRAM. THE VALUE OF OPERATOR PROGRAM, BY THE WAY, LIES IN THE FACT THAT IT INVOLVES THE FASTER TAPE INPUT TO THE CENTRAL PROCESSING UNIT AS AGINST CARD INPUT AS WELL AS COMPILATION AND COMPUTATION IN SAME RUN. THE TAPE IS FED INTO THE MACHINE WH+CH THEN CONVERTS THE PROGRAM TO BINARY FORM (SHARE ASSEMBLY PROGRAM), EXECUTES THE COMPUTATIONS AT THE RATE OF 40,000 MACHINE CYCLES PER SECOND, CONVERTS THE RESULTS TO THE FORM DESIRED (USUALLY DECIMAL NOTATION), RECORDS THEM ON TAPE FOR LATER OFF-LINE PRINTOUT, RECORDS THE BINARY FORM ON TAPE FOR A PUNCHED CARD OUTPUT IF DESIRED, AND MAKES AN ON-LINE RECORD OF THE SHARE ASSEMBLER STATISTICS TOGETHER WITH A RECORD OF TIME REQUIRED FOR EACH PHASE OF OPERATION. ERROR STOPS ARE HANDLED BY THE MACHINE OPERATOR IN THAT HE INITIATES THE SO-CALLED POST-MORTEM FOR INTERMEDIATE RESULTS.

THE FIRST FIVE OPERATIONS HAVE BEEN DESCRIBED, NAMELY THE RUN, B+N, CST, AND SAP CA-DS. THE COMPUTING STOPS ON AN HLT CARD WHICH ALLOWS THE POST-MORTEM AND PRINTOUT OF RESULTS. THE FINAL CARD OF THE SAP DECK IS AN END CARD WITH THE VARIABLE FIELD REFERRING TO THE START OF THE PROGRAM, IN THIS CASE START. ALL STORAGE ASSIGNMENTS AND COMPUTATIONS MUST BE COMPLETED BEFORE END IS EXECUTED. IF FURTHER PROGRAMS ARE TO BE RUN WITH THIS SAP DECK, ANOTHER CST CARD IS NEEDED AS IS AN ORIGIN CARD SUCH AS ORG H FOR WRITING OVER THE OLD VALUES IN CORE STORAGE OF RESONANCE AND COULOMBIC INTEGRALS WITH THE NEW INPUT DATA. FOLLOWING THIS WILL BE A DEC CARD OR CARDS WITH THE NEW DATA. H MUST NOT BE DEFINED IN THIS NEW DECK. IF THIS IS THE ONLY TYPE OF ALTERATION

```
02376  0 60100 0 02552          STO H+11
02377  0 50000 0 02572          CLA NEW+2
02400  0 60100 0 02554          STO H+13
02401  0 60100 0 02560          STO H+17
02402  0 50000 0 02573          CLA NEW+3
02403  0 60100 0 02562          STO H+19
02404  0 60100 0 02566          STO H+23
02405  0 02000 0 01756          TRA CONTRL
02406 +202500000000      TWALF DEC 2.5
02407 +200546314631      SEVEN DEC .7
02410 +201400000000          I DEC 1.
02411 +202400000000       TWOP DEC 2.
02412 +201400000000        ONE DEC 1.
02413 +177614223351          M DEC .387
02414 +200516254020          B DEC .653
                02415 CLOUD1 LIB
02457  0 00000 0 00017    FEEN PZE 15
02460 +163643334272      DELTA DEC .0001
02461  0 00000 0 00005   COUNT PZE 5
02462  0 00000 0 00004    SIZE PZE 4
02463  0 02000 4 00001   UNDFL TRA 1,4
02464  0 00000 0 00000   OVERF HTR
02465  0 00000 0 00000   DCLON HTR
02466  0 50000 0 02500   NPBIT CLA TOUGH
02467  0 30000 0 02410         FAD I
02470  0 60100 0 02500         STO TOUGH
02471  0 02000 4 00001         TRA 1,4
02472  0 00000 0 00003   THREE PZE 3
02473  0 00000 0 00002   SIGMA PZE 2
02474  0 00000 0 00017     ZIP PZE 15
02475  0 00000 0 00005     RCN PZE 5
02476  0 00000 0 00000    CTIT PZE
02477  0 00000 0 00000       R PZE
02500  0 00000 0 00000   TOUGH PZE
                02501      TRI BSS 25
                02532        E BSS 5
```

TO BE MADE ON THE PROGRAM, AN (END START) CARD IS NEXT.

WHEN ALL SETS OF INPUT DATA HAVE BEEN THUS ACCOUNTED FOR, A POST-MORTEM DECK IS STARTED WITH A CARD REFERRING TO THE FIRST SAP DECK, IDENTICAL LABELING BEING REQUIRED. NEXT COMES A POST-MORTEM REQUEST WITH THE RANGE OF CORE STORAGE DESIRED FOR PRINTED OUTPUT, THE TYPE OF NOTATION, THE TYPE OF ARITHMETIC, AND A DESIGNATION FOR ON-LINE OR OFF-LINE PRINTING. PMR CTIT,ASE+12,FLO,FPR IS THE CARD USED IN THE PRINTED OUTPUT FOR THIS PROGRAM. IT IS POSSIBLE TO OBTAIN MORE ELABORATE OUTPUT, LISTING THE RESULTS IN TABULAR FORM UNDER PRESCRIBED HEADINGS. ONE SUBROUTINE WHICH WILL AID IN DOING THIS IS UABDC1.

THE NEXT CARD REQUIRED IS A RIP CARD, IN FACT, THERE MUST BE A RIP CARD FOR EACH DECK INVOLVED. FOR THIS PROGRAM, CONSISTING OF TWO SETS OF DATA, WE WOULD HAVE

```
RIP CNTRC
RIP HDIAG
RIP N377-HBUT-SCF
BGN N377-HBUT-SCF
CON 1
CON 1
XPM N377-HBUT-SCF
CLR
RIP CNTRC
RIP HDIAG
RIP N377-HBUT-SCF
RIP N377-HBUT-SCF2
BGN N377-HBUT-SCF
CON 1
CON 1
XPM N377-HBUT-SCF
TER N377-307-JORDAN
```

THESE INSTRUCTIONS CAUSE THE MACHINE TO READ INTO CORE STORAGE THE BINARY FORM OF ALL DECKS REFERRED TO BY RIP,

```
02537 -200400000000          H DEC -.5,2.5,0.,0.,0.            THE FORMAT FOR THE TITLES BEING SUCH THAT
02540 +202500000000
02541 +000000000000
02542 +000000000000
02543 +000000000000
02544 +202500000000            DEC 2.5,-.1,.7,0.,0.            THE PROGRAMMER AND PROBLEM NUMBER CAN
02545 -175631463146
02546 +200546314631
02547 +000000000000
02550 +000000000000
02551 +000000000000            DEC 0.,.7,0.,.7,0.              BE EASILY IDENTIFIED.
02552 +200546314631
02553 +000000000000
02554 +200546314631
02555 +000000000000
02556 +000000000000            DEC 0.,0.,.7,0.,1.                   PROGRAM OPERATION STARTS THROUGH THE
02557 +000000000000
02560 +200546314631
02561 +000000000000
02562 +201400000000
02563 +000000000000            DEC 0.,0.,0.,1.,0.              INTERPRETATION OF THE BGN CARD, THE
02564 +000000000000
02565 +000000000000
02566 +201400000000
02567 +000000000000
                 02570    NEW BSS 4          CONTINUE (CON) CARDS ARE ASSOCIATED WITH THE  ERROR STOP
                 02574     F1 BSS 3          PHASE OF OPERATION, XPM INITIATES POSTMORTEM EXECUTION
                 02577     F2 BSS 3          AND THE TER CARD REFERS TO THE TERMINATION OF THE RUN AND
                 02602     F3 BSS 3          MUST HAVE THE SAME TITLE AS THE RUN CARD.  THE DETAILS OF
                 02605     F4 BSS 3          THE MANY REQUIREMENTS AND RAMIFICATIONS OF THESE
                 02610     C1 BSS 3          PROCEDURES CAN BE FOUND IN THE USERS REFERENCE MANUAL FOR
                 02613     C2 BSS 3          THE M.I.T. AUTOMATIC OPERATOR PROGRAM, MEMO CC-75-1.
                 02616     C3 BSS 3
                 02621     C4 BSS 3               NOTICE THAT ONLY A SELECTED RANGE OF CORE STORAGE IS
                 02624     C5 BSS 3          PRINTED, ACCORDING TO THE PMR FROM LOCATION CTIT
                 02627  ORDER BSS 4          TO ASE+12.  OTHER PMR CARDS CAN BE ADDED FOR VARIOUS
```

```
                02633     Q1 BSS 3           OTHER RANGES.  ALSO IT IS POSSIBLE TO CHANGE THE NATURE
                02636     Q2 BSS 3           OF THE COMPUTATIONS THEMSELVES VERY EASILY BY USING OCTAL
                02641     Q3 BSS 3           CORRECTION CARDS OR BY ADDING A SAP DECK WITH AN ORIGIN
                02644     Q4 BSS 3           (ORG) CARD.  IN FACT, THIS IS THE METHOD USED TO  READ IN
                02647     Q5 BSS 3           NEW SETS OF COULOMBIC AND RESONANCE INTEGRALS, AS IS SEEN
                02652     ER BSS 15          BY THE ORG H AND DEC CARDS OUTSIDE THE MAIN SAP DECK.
                02671    ERT BSS 15
                02710     AE BSS 13
                02725    ASE BSS 13
                01750        END START

ARE ASSEMBLER STATISTICS

PE  TOTAL      1 FAIL      2 FAIL      3 FAIL      4 FAIL
P     347           0           0           0           0
B      70           0           0           0           0
L'    381           0           0           0           0

RECT READ-IN STATUS,       PROGRAM GOOD,     SYMBOLS GOOD

MBER OF OFF-LINE PRINT RECORDS      378

MBER OF SYMBOLS,  DEF    74,DEFOP     0,UNDEF     0
```

CST
SAP N377-HBUT-SCF2

```
                  02537          ORG H
 02537 -200400000000             DEC -.5,1.,0.,0.,0.
 02540 +201400000000
 02541 +000000000000
 02542 +000000000000
 02543 +000000000000
 02544 +201400000000             DEC 1.,-.1,1.,0.,0.
 02545 -175631463146
 02546 +201400000000
 02547 +000000000000
 02550 +000000000000
 02551 +000000000000             DEC 0.,1.,0.,1.,0.
 02552 +201400000000
 02553 +000000000000
 02554 +201400000000
 02555 +000000000000
 02556 +000000000000             DEC 0.,0.,1.,0.,1.
 02557 +000000000000
 02560 +201400000000
 02561 +000000000000
 02562 +201400000000
 02563 +000000000000             DEC 0.,0.,0.,1.,0.
 02564 +000000000000
 02565 +000000000000
 02566 +201400000000
 02567 +000000000000
                  01750          END START

ARE ASSEMBLER STATISTICS

PE   TOTAL      1 FAIL      2 FAIL      3 FAIL      4 FAIL
P        7           0           0           0           0
B        0           0           0           0           0
L        7           0           0           0           0

RECT READ-IN STATUS,      PROGRAM GOOD,     SYMBOLS GOOD

MBER OF OFF-LINE PRINT RECORDS       35
```

```
MBER OF SYMBOLS,  DEF    74,DEFOP      0,UNDEF     0
```

```
PMD N377-HBUT-SCF
CLR
RIP CNTRC
RIP HDIAG
RIP N377-HBUT-SCF
BGN N377-HBUT-SCF
CON 1
```

```
**** CON 1
     XPM N377-HBUT-SCF
     CLR
     RIP CNTRC
     RIP HDIAG
     RIP N377-HBUT-SCF
     RIP N377-HBUT-SCF2
     BGN N377-HBUT-SCF
     CON 1
```

```
**** CON 1
     XPM N377-HBUT-SCF
     TER N377-307-JORDAN
```

```
HASE 3, POST MORTEM, RESULTS OF RUN          N377-307-JORDAN*00
     CLR
     RIP CNTRC
     RIP HDIAG
     RIP N377-HBUT-SCF
     BGN N377-HBUT-SCF
     CON 1
```

```
*** CON 1
     XPM N377-HBUT-SCF


           REM AC WAS   +,Q=0,P=0, 2 00544 1 37244  +.695676118E+00
           REM IR1=/3=3,IR2=/0=0,IR4=/75434=31516
           REM LITES ON
           REM SWITCHES DOWN
           REM MQ OR C(5) = +0 00000 0 00000 = +.000000000E-38
           REM ILC=/0=0
```

```
      ORG 1342
 CTIT DEC +.500000000E+01                                      02476
    R DEC +.0000000864E-38                                     02477
TOUGH DEC +.200000000E+01                                      02500
  TRI DEC +.253974208E+01,+.0000000000E-38                     02501
      DEC +.126180888E+01,+.0000000000E-38                     02503
      DEC +.0000000000E-38,-.195651233E-01                     02505
      DEC +.0000000000E-38,+.0000000000E-38                    02507
      DEC +.0000000000E-38,-.129042492E+01                     02511
      DEC +.0000000000E-38,+.0000000000E-38                    02513
      DEC +.0000000000E-38,+.0000000000E-38                    02515
      DEC -.309156104E+01                                      02517
      DEC +.0000000000E-38                                     02520
      REP 1,9


    E DEC -.309156104E+01,-.129042492E+01                      02532
      DEC -.195651233E-01,+.126180888E+01                      02534
      DEC +.253974208E+01                                      02536
    H DEC -.500000000E+00,+.268846392E+01                      02537
      DEC +.0000000000E-38,+.0000000000E-38                    02541
      DEC +.0000000000E-38,+.268846392E+01                     02543
      DEC -.999999992E-01,+.752769902E+00                      02545
      DEC +.0000000000E-38,+.0000000000E-38                    02547
      DEC +.0000000000E-38,+.752769902E+00                     02551
      DEC +.0000000000E-38,+.908598199E+00                     02553
      DEC +.0000000000E-38,+.0000000000E-38                    02555
      DEC +.0000000000E-38,+.908598199E+00                     02557
      DEC +.0000000000E-38,+.939595550E+00                     02561
      DEC +.0000000000E-38,+.0000000000E-38                    02563
      DEC +.0000000000E-38,+.939595550E+00                     02565
      DEC +.0000000000E-38                                     02567
```

```
  NEW DEC +.102502016E+01,+.752758078E+00                       02570
      DEC +.908664278E+00,+.939534626E+00                       02572
   F1 DEC +.0000000000E-38,+.655321747E+00                      02574
      DEC +.113066127E+01                                       02576
   F2 DEC +.0000000000E-38,-.238590961E+01                      02577
      DEC +.393467128E-00                                       02601
   F3 DEC +.0000000000E-38,-.385634532E+01                      02602
      DEC +.163083344E-00                                       02604
   F4 DEC +.0000000000E-38,-.287159559E+01                      02605
      DEC +.603338360E-01                                       02607
   C1 DEC +.0000000000E-38,+.181849831E-00                      02610
      DEC +.637130402E+00                                       02612
   C2 DEC +.0000000000E-38,+.119170148E-00                      02613
      DEC +.720378674E+00                                       02615
   C3 DEC +.0000000000E-38,-.433877259E-00                      02616
      DEC +.250689867E-00                                       02620
   C4 DEC +.0000000000E-38,-.701275743E+00                      02621
      DEC +.103905355E-00                                       02623
   C5 DEC +.0000000000E-38,-.522199168E+00                      02624
      DEC +.384405210E-01                                       02626
ORDER DEC +.961292438E+00,+.257772833E-00                       02627
      DEC +.660631231E+00,+.740399569E+00                       02631
   Q1 DEC +.0000000000E-38,+.330693608E-01                      02633
      DEC +.405935144E-00                                       02635
   Q2 DEC +.0000000000E-38,+.142015242E-01                      02636
      DEC +.518945433E+00                                       02640
   Q3 DEC +.0000000000E-38,+.188249476E-00                      02641
      DEC +.6[illegible]8454096E-01                                       02643
   Q4 DEC +.0000000000E-38,+.491787666E-00                      02644
      DEC +.107963229E-01                                       02646
   Q5 DEC +.0000000000E-38,+.272691968E-00                      02647
      DEC +.147767366E-02                                       02651
   ER DEC -.0000000000E-38,+.417272126E-01                      02652
      DEC +.103097055E+01,-.0000000000E-38                      02654
      DEC +.179196095E-01,+.131798754E+01                       02656
      DEC -.0000000000E-38,+.237534859E-00                      02660
```

```
     DEC +.159611131E-00,-.0000000000E-38                                  02662
     DEC +.620542049E+00,+.274198755E-01                                   02664
     DEC -.0000000000E-38,+.344085147E-00                                  02666
     DEC +.375290998E-02                                                   02670
 ERT DEC -.0000000000E-38,+.834544263E-01                                  02671
     DEC +.206194111E+01,-.0000000000E-38                                  02673
     DEC +.358392190E-01,+.263597509E+01                                   02675
     DEC -.0000000000E-38,+.475069719E-00                                  02677
     DEC +.319222262E-00,-.0000000000E-38                                  02701
     DEC +.124108409E+01,+.548397511E-01                                   02703
     DEC -.0000000000E-38,+.688170298E+00                                  02705
     DEC +.750581997E-02                                                   02707
  AE DEC +.214539551E+01,+.0000000000E-38                                  02710
     DEC +.0000000000E-38,+.267181429E+01                                  02712
     DEC +.0000000000E-38,+.0000000000E-38                                 02714
     DEC +.794291988E+00,+.0000000000E-38                                  02716
     DEC +.0000000000E-38,+.129592384E+01                                  02720
     DEC +.0000000000E-38,+.0000000000E-38                                 02722
     DEC +.695676118E+00                                                   02724
 ASE DEC +.214539551E+01,+.0000000000E-38                                  02725
     DEC +.0000000000E-38,+.267181429E+01                                  02727
     DEC +.0000000000E-38,+.0000000000E-38                                 02731
     DEC +.794291988E+00,+.0000000000E-38                                  02733
     DEC +.0000000000E-38,+.129592384E+01                                  02735
     DEC +.0000000000E-38,+.0000000000E-38                                 02737
     DEC +.695676118E+00                                                   02741


CLR
RIP CNTRC
RIP HDIAG
RIP N377-HBUT-SCF
RIP N377-HBUT-SCF2
BGN N377-HBUT-SCF
CON 1
```

```
*** CON 1
    XPM N377-HBUT-SCF
          REM AC WAS   +,Q=0,P=0, 2 00544 1 41705  +.695685900E+00
          REM IR1=/3=3,IR2=/0=0,IR4=/75434=31516
          REM LITES ON
          REM SWITCHES DOWN
          REM MQ OR C(5) = +0 00000 0 00000 = +.0000000000E-38
          REM ILC=/0=0



          ORG 1342
     CTIT DEC +.500000000E+01                                     02476
        R DEC +.0000000864E-38                                    02477
    TOUGH DEC +.200000000E+01                                     02500
      TRI DEC +.253974649E+01,+.0000000000E-38                    02501
          DEC +.126180949E+01,+.0000000000E-38                    02503
          DEC +.0000000000E-38,-.195653975E-01                    02505
          DEC +.0000000000E-38,+.0000000000E-38                   02507
          DEC +.0000000000E-38,-.129042500E+01                    02511
          DEC +.0000000000E-38,+.0000000000E-38                   02513
          DEC +.0000000000E-38,+.0000000000E-38                   02515
          DEC -.309156560E+01                                     02517
          DEC +.0000000000E-38                                    02520
          REP 1,9



        E DEC -.309156560E+01,-.129042500E+01                     02532
          DEC -.195653975E-01,+.126180949E+01                     02534
          DEC +.253974649E+01                                     02536
        H DEC -.500000000E+00,+.268846854E+01                     02537
          DEC +.0000000000E-38,+.0000000000E-38                   02541
          DEC +.0000000000E-38,+.268846854E+01                    02543
          DEC -.999999992E-01,+.752771198E+00                     02545
          DEC +.0000000000E-38,+.0000000000E-38                   02547
```

```
      DEC +.000000000E-38,+.752771198E+00                                02551
      DEC +.000000000E-38,+.908590890E+00                                02553
      DEC +.000000000E-38,+.000000000E-38                                02555
      DEC +.000000000E-38,+.908590890E+00                                02557
      DEC +.000000000E-38,+.939602293E+00                                02561
      DEC +.000000000E-38,+.000000000E-38                                02563
      DEC +.000000000E-38,+.939602293E+00                                02565
      DEC +.000000000E-38                                                02567
  NEW DEC +.102502004E+01,+.752758480E+00                                02570
      DEC +.908662170E+00,+.939536593E+00                                02572
   F1 DEC +.000000000E-38,+.655320845E+00                                02574
      DEC +.113066098E+01                                                02576
   F2 DEC +.000000000E-38,-.238591277E+01                                02577
      DEC +.393465876E-00                                                02601
   F3 DEC +.000000000E-38,-.385638248E+01                                02602
      DEC +.163081713E-00                                                02604
   F4 DEC +.000000000E-38,-.287164250E+01                                02605
      DEC +.603335607E-01                                                02607
   C1 DEC +.000000000E-38,+.181848116E-00                                02610
      DEC +.637130692E+00                                                02612
   C2 DEC +.000000000E-38,+.119168859E-00                                02613
      DEC +.720378808E+00                                                02615
   C3 DEC +.000000000E-38,-.433873742E-00                                02616
      DEC +.250689184E-00                                                02620
   C4 DEC +.000000000E-38,-.701275885E+00                                02621
      DEC +.103904363E-00                                                02623
   C5 DEC +.000000000E-38,-.522202774E+00                                02624
      DEC +.384403634E-01                                                02626
ORDER DEC +.961292162E+00,+.257773876E-00                                02627
      DEC +.660625778E+00,+.740404658E+00                                02631
   Q1 DEC +.000000000E-38,+.330687367E-01                                02633
      DEC +.405935513E-00                                                02635
   Q2 DEC +.000000000E-38,+.142012172E-01                                02636
      DEC +.518945626E+00                                                02640
   Q3 DEC +.000000000E-38,+.188246423E-00                                02641
      DEC +.628450676E-01                                                02643
```

```
 Q4 DEC +.0000000000E-38,+.491787862E-00                         02644
    DEC +.107961168E-01                                          02646
 Q5 DEC +.0000000000E-38,+.272695735E-00                         02647
    DEC +.147766153E-02                                          02651
 ER DEC -.0000000000E-38,+.417264461E-01                         02652
    DEC +.103097330E+01,-.0000000000E-38                         02654
    DEC +.179192306E-01,+.131799033E+01                          02656
    DEC -.0000000000E-38,+.237531122E-00                         02660
    DEC +.159610539E-00,-.0000000000E-38                         02662
    DEC +.620542593E+00,+.274193999E-01                          02664
    DEC -.0000000000E-38,+.344090065E-00                         02666
    DEC +.375288569E-02                                          02670
ERT DEC -.0000000000E-38,+.834528923E-01                         02671
    DEC +.206194660E+01,-.0000000000E-38                         02673
    DEC +.358384612E-01,+.263598066E+01                          02675
    DEC -.0000000000E-38,+.475062245E-00                         02677
    DEC +.319221079E-00,-.0000000000E-38                         02701
    DEC +.124108518E+01,+.548387998E-01                          02703
    DEC -.0000000000E-38,+.688180133E+00                         02705
    DEC +.750577139E-02                                          02707
 AE DEC +.214539948E+01,+.0000000000E-38                         02710
    DEC +.0000000000E-38,+.267181912E+01                         02712
    DEC +.0000000000E-38,+.0000000000E-38                        02714
    DEC +.794283322E+00,+.0000000000E-38                         02716
    DEC +.0000000000E-38,+.129592397E+01                         02720
    DEC +.0000000000E-38,+.0000000000E-38                        02722
    DEC +.695685900E+00                                          02724
ASE DEC +.214539948E+01,+.0000000000E-38                         02725
    DEC +.0000000000E-38,+.267181912E+01                         02727
    DEC +.0000000000E-38,+.0000000000E-38                        02731
    DEC +.794283322E+00,+.0000000000E-38                         02733
    DEC +.0000000000E-38,+.129592397E+01                         02735
    DEC +.0000000000E-38,+.0000000000E-38                        02737
    DEC +.695685900E+00                                          02741
```

```
TER N377-307-JORDAN
EOT
```

BIOGRAPHICAL DATA

Name in Full	Maurice Donald Jordan, Jr.
Date of Birth	August 17, 1926
Place of Birth	Lewiston, Maine
Secondary education	Portland, Maine

Collegiate institutions attended	Dates	Degree
Worcester Polytechnic Institute	1944–1946	
Bowdoin College	1948–1950	A.B.
University of New Hampshire	1954–1958	Ph.D.

Positions held

Chemist, S. D. Warren Co., Boston, Mass.