A STUDY OF THE USE OF A STEEPEST DESCENT TECHNIQUE IN THE

SOLUTION OF THE HARTREE-FOCK EQUATIONS AND ITS APPLICATION

TO SELECTED SYSTEMS

by

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I.   Introduction

In the approximate self-consistent field (SCF) theory (1) the
n doubly occupied (closed shell system) orbitals of a one-determinant
wave function (Hartree-Fock) are combinations of m basic orbitals
(basis set). The approximate SCF equations determine the n linear
combinations which give the lowest total energy. (2)   Therefore,
these orbitals give the best possible representation of the true SCF
orbitals (3), using the basis set of one-electron functions.

In the present context of molecular theory, the SCF orbitals
are molecular orbitals (MO) while the basic orbitals are atomic
orbitals (AO). This approximation is the linear combination of atomic
orbitals (LCAO).

To obtain the individual MO's requires repeated solution (an
iterative process) of matrix eigenvalue equations. A brief description
of the orthodox SCF method is in order. The Hartree-Fock equations
(4,5) are

$$\underset{\sim\sim}{FA} = \underset{\sim\sim}{A} \varepsilon \qquad\qquad (1)$$

where $\underset{\sim}{A} = (A, B, \ldots X)$ is the row matrix of n occupied orbitals;
is an m x m diagonal matrix whose elements are the orbital energies
ε_A, $\varepsilon_B \ldots \varepsilon_X$; and $\underset{\sim}{F} = \underset{\sim}{h} + \underset{\sim}{G}$ is the Hartree-Fock matrix operator.
Matrix h is the one-electron matrix operator for an electron in the
field of the bare nuclei, and G is the total electron interaction
matrix operator, which includes both exchange and Coulomb terms.

The orbital energies and total energy are

$$\varepsilon_A = \langle A/F/A \rangle \qquad\qquad (2)$$

$$E = \sum_A \langle A/2F - G/A \rangle$$

-1-

$$= 2 \sum_A \varepsilon_A - \sum_A <A/G/A> \tag{3}$$

Upon application of the LCAO approximation by using a set of m basic

orbitals, $\underset{\sim}{a} = (ab...)$, the n occupied orbitals are expressed as

$\underset{\sim}{A} = \underset{\sim}{a} \underset{\sim}{T}$, where $\underset{\sim}{T}$ is an m x m matrix.

Equation (1) then takes the approximate form

$$\underset{\sim}{F} \underset{\sim}{T} = \underset{\sim}{T} \underset{\sim}{\varepsilon} \quad (\underset{\sim}{\varepsilon} \text{ diagonal}) \tag{4}$$

The definition of the Hartree-Fock matrix is completed by

$$h_{ab} = <a/h/b>$$

and

$$G_{ab} = \sum_{r,s} R_{rs} [2<as/g/br> - <as/g/rb>]$$

where for our purpose $\underset{\sim}{R} = \underset{\sim}{T}\underset{\sim}{T}^t$ and $g = e^2/r_{12}$. Consequently, equations

(2) and (3) become

$$\varepsilon_A = <\underset{\sim}{T}^t \underset{\sim}{F} \underset{\sim}{T}>_A \tag{5}$$

$$E = 2Tr(\underset{\sim}{R}\underset{\sim}{F}) - Tr(\underset{\sim}{R}\underset{\sim}{G}) \tag{6}$$

$\underset{\sim}{R}$ is one-half the charge density and bond order matrix.

Equations (4), (5), and (6) demonstrate that, while the orbital

energies and eigenvalue equations depend on the orbital-coefficient

matrix $\underset{\sim}{T}$, the total energy depends only on $\underset{\sim}{R}$. More will be said

concerning this later.

To summarize, the orthodox Hartree-Fock method involves making

an initial "guess" at $\underset{\sim}{R}$ followed by successive refinements achieved

by direct diagonalization of the Hartree-Fock matrix until convergence

is achieved.

The orthodox Hartree-Fock method has two major objections.

First, as was demonstrated earlier it does not generate physically

relevant information, i.e., the total energy (and all other physical properties of a system) does not depend on the individual MO's (the solutions directly obtained) but on R. Secondly, some systems do not achieve convergence, i.e., the energy oscillates between two extremes, neither of which is close to the energy minimum. This objection is encountered with both π-electron and all-valence-electron systems, with particular difficulty in the latter (6,7).

McWeeny (8,9) has developed an alternative to the orthodox method which seems to overcome the above-stated objections. R is generated directly, and convergence is apparently achieved for all systems.

The objective of this paper is to describe McWeeny's method and to report on results obtained with its use. The systems with which we worked included both π-electron and all-valence-electron systems. The π-electron systems were p-benzoquinone and calicene. The all-valence-electron systems were the calicene dianion, several configurations of the Cl_2-benzene charge-transfer complex, and a study of selectivity in propylene, nitrobenzene, and m-chloronitrobenzene.

II. The Mathematical Development of McWeeny's Method

In the past, theoreticians in chemistry and physics have sought a method of solving the Hartree-Fock equations which would yield physically relevant information and which, in the case of certain recalcitrant systems, would yield convergent physical properties. McWeeny's "steepest descent" method (10,11) fulfills these requirements.

The objective of the method is to systematically change R (one-half the charge density and bond order matrix) in such a way that E (total electronic energy) is rapidly reduced to a minimum. Before giving further details of McWeeny's method, the reader should be apprised of certain background information.

The total electronic energy can be represented as

$$E = 2 \, \text{Tr} \, (hR) + \text{Tr} \, (GR) \tag{7}$$

subject to

$$R^2 = R, \quad (\text{Tr} \, R = n)$$

To first-order

$$\delta E = 2 \, \text{Tr}(h\delta R) + \text{Tr}(G\delta R) + \text{Tr}(\delta G R) = 0 \tag{8}$$

where

$$G = G(R), \quad \text{Tr}(\delta G R) = \text{Tr}(G(\delta R)R) = \text{Tr}(G(R)\delta R)$$

Therefore,

$$\delta E = 2 \, \text{Tr}(h\delta R) + 2 \, \text{Tr}(G\delta R) = 2 \, \text{Tr}(F\delta R) = 0 \tag{9}$$

$$\epsilon = 2 \, \text{Tr}(FR) = \text{stationary value} \tag{10}$$

where ϵ is merely the sum of the orbital energies (ϵ). Now, to second-order with idempotency still preserved,

$$\delta R = (V + V^+) + (VV^+ - V^+V) \ldots \tag{11}$$

where

$$\underset{\sim}{V} = (\underset{\sim}{1}-\underset{\sim}{R}) \underset{\sim}{\Delta} \underset{\sim}{R}$$

with Δ an arbitrary, nonsingular m x m matrix.

We can now proceed with the development of McWeeny's method. An arbitrary, idempotent $\underset{\sim}{R}$ is first chosen (e.g., that of a Hückel calculation). From (9), (10), and (11),

$$\delta E \text{ first-order} = \delta \epsilon = 4\text{Tr}[\underset{\sim}{R}\underset{\sim}{F}(\underset{\sim}{1}-\underset{\sim}{R})\underset{\sim}{\Delta}] = 4\text{Tr}[(\underset{\sim}{1}-\underset{\sim}{R})\underset{\sim}{F}\underset{\sim}{R}]^{+}\underset{\sim}{\Delta} = 0 \qquad (12)$$

Δ must be chosen in order to descend the energy surface as rapidly as possible.

A vector can be associated with the m^2 elements of an m x m matrix, and we define a scalar product as

$$\underset{\sim}{A} \cdot \underset{\sim}{B} = \underset{r,s}{\Sigma} A_{rs} B_{rs} = \underset{r,s}{\Sigma} A_{sr}^{+} B_{rs} = \text{Tr} \left(\underset{\sim}{A}^{+}\underset{\sim}{B}\right)$$

For fixed $\underset{\sim}{B}$ the scalar product takes its greatest negative value when $\underset{\sim}{A}$ is in its antiparallel position, $\underset{\sim}{A} = -\lambda\underset{\sim}{B}$.

Consequently, from (12) E takes its greatest reduction when $\underset{\sim}{\Delta} = -\lambda(\underset{\sim}{1}-\underset{\sim}{R})\underset{\sim}{F}\underset{\sim}{T}$, and $\underset{\sim}{V} = (\underset{\sim}{1}-\underset{\sim}{R})\underset{\sim}{\Delta}\underset{\sim}{R} = -\lambda(\underset{\sim}{1}-\underset{\sim}{R})\underset{\sim}{F}\underset{\sim}{R}$. Therefore, the change in R corresponding to the steepest descent along the energy surface is

$$\delta \underset{\sim}{R} = -\lambda(\underset{\sim}{S}+\underset{\sim}{S}^{+}) + \lambda^2 (\underset{\sim}{S}\underset{\sim}{S}^{+} - \underset{\sim}{S}^{+}\underset{\sim}{S}) \ldots \qquad (13)$$

where $\underset{\sim}{S} = (\underset{\sim}{1}-\underset{\sim}{R})\underset{\sim}{F}\underset{\sim}{R}$.

$$\delta\underset{\sim}{R} = -\lambda\underset{\sim}{L} - \lambda^2 \underset{\sim}{L}\underset{\sim}{M} \ldots \qquad (14)$$

where $\underset{\sim}{L} = \underset{\sim}{S} + \underset{\sim}{S}^{+}$ and $\underset{\sim}{M} = \underset{\sim}{S}-\underset{\sim}{S}T$.

$$[(\underset{\sim}{1}-\underset{\sim}{R}) \underset{\sim}{R} = \underset{\sim}{0}]$$

This correction satisfies the idempotency condition of (7) to second-order and therefore determines not only the slope of the energy surface (see eq. 12) in the direction of increasing λ but also its curvature. It is, therefore, possible to determine a value $\lambda_{opt.}$ which corresponds to a minimum in the direction of steepest descent (see Fig. 1, page 6).
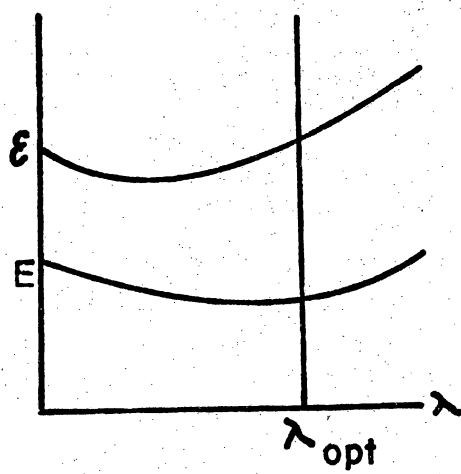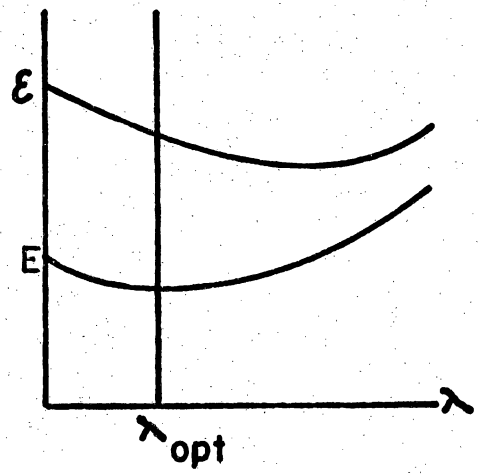
Fig. 1. Section through the energy surfaces: (a) The simple
Hartree-Fock procedure predicts too small a change; (b) it leads
to divergence.

Thus, the total energy change to second-order is

$$\delta E = 2Tr(-\lambda \underset{\sim}{L} - \lambda^2 \underset{\sim\sim}{LM})\underset{\sim}{F} + Tr(\lambda^2 \underset{\sim}{L} \underset{\sim}{G}(L)) = 0 \qquad (15)$$

setting

$$\partial(\delta E)/\partial \lambda = 0. \quad \lambda_{opt.} = -t/(2m-m') \qquad (16)$$

where

$$t = Tr(\underset{\sim\sim}{FL}) \qquad m = Tr(\underset{\sim\sim\sim}{FLM}) \qquad m' = Tr(\underset{\sim\sim}{LG(L)})$$

The correction (14) with $\lambda = \lambda_{opt.}$ results in the best 1-descent

approximation to $\underset{\sim}{R}$ and consequently E. This procedure is repeated

until $\underset{\sim}{R}$ and E do not change upon further iteration within an arbit-

rary limit.

Although (14) maintains idempotency to second-order, repeated

addition of $\delta \underset{\sim}{R}$'s results in the loss of idempotency, which decreases

the rapidity of achieving convergence. Idempotency is re-established

by the iterative application of

$$\underset{\sim}{R}_{j+1} = 3\underset{\sim}{R}_j^3 - 2\underset{\sim}{R}_j^2 \qquad (17)$$

Also, McWeeny alleges that averaging the S-matrices of two

consecutive iterations and employing the result in the next iteration

results in more rapid convergence.

III. The Implementation of McWeeny's Method

The preceding development of McWeeny's use of the "steepest descent" method to solve the Hartree-Fock equations appears to demonstrate that the method should result in convergence for all physically realistic systems, including those systems which do not achieve convergence with the orthodox method (see I). Also, those systems which do achieve convergence with the orthodox method should do so in fewer iterations with the McWeeny method. To test these contentions, several systems, both π-electron and all-valence-electron systems, were used as examples for study. Some of these systems had not converged with the orthodox method. What is to follow is a narration of what was involved in utilizing McWeeny's method.

To gain an initial familiarity with McWeeny's method we considered a WATFIV program for π-electron systems which normally present fewer difficulties in achieving convergence than all-valence-electron systems. As will be shown shortly, this normality was proven to be somewhat absent. But to continue, the zero-differential-overlap approximation was applied to all repulsion integrals. One-half the charge density and bond order matrix resulting from a simple Hückel calculation was used as a first approximation to $\underset{\sim}{R}$. Slater-type 2p-orbitals were used for the basis set.

To begin our investigation of the efficiency of McWeeny's method, in solving π-electron systems, we used p-benzoquinone. With computer runs of 10, 20, and 30 iterations, we could not obtain convergence. After proceeding monotonically for three iterations towards a minimum,

the electronic energy and $\underset{\sim}{R}$ moved nonmonotonically towards and away
from a minimum without finally converging to that minimum.

By increasing the number of iterations from 3 to 5 in using
equation 17, we observed a reduction in the above-described nonmono-
tonic behavior. Because we did not observe further improvement upon
going to 7 iterations, we abandoned further investigation of the
technique. We also increased the periodicity of the application of
equation 17 still without achieving convergence.

Upon failing to obtain convergence by exclusive use of McWeeny's
method, we investigated variations of the method.

When an iterative process fails to converge, a well-established
technique is to average a variable resulting from two consecutive
iterations and to use the resultant in the following iteration. This
is repeated periodically throughout the iterative process. We applied
this technique by averaging the $\underset{\sim}{R}$'s. We observed no appreciable
improvement in the results.

Because the energy surface with which he was working was nonlinear,
McWeeny used a quadratic dependence in λ as an approximation to δE
(see equation 15). We attempted to adapt a linear adjustment to λ.
After calculating λ for an iteration, fractional parts of it, ranging
from -1 to +1 in .1 increments, were taken. After determining which
fraction of $\lambda_{opt.}$ gives the highest negative δE, the resulting δR was
made idempotent with equation 17 and was used to calculate a new $\lambda_{opt.}$
in the next iteration. This was repeated throughout the iterative
process. This is a commonly used technique in nonlinear problems and
is an extension of finding a steepest descent (see II). Again, no
discernable improvement in results was observed.

As was explained in section II, McWeeny reported that averaging

the S-matrices (which is analogous to the r-matrix in his paper) of

two consecutive iterations and using the resultant in the following

iteration gave more rapid convergence in eigenvalue problems. After

employing this technique in the p-benzoquinone calculations, we

observed no improvement in the results.

The technique which finally brought forth sufficiently satisfactory

results to evoke a "HAZZAH!" was indirectly suggested to us in a paper

by Amos (12). He reported that he had used the orthodox method in

conjunction with McWeeny's method to confirm the obtainment of

convergence. After using sufficiently many McWeeny iterations to

give apparent convergence, he followed them with several standard

diagonalizations (the orthodox method). If he observed no further

change, he concluded that convergence had indeed been obtained.

In addition, Fletcher (13) observed that the difficulty with

McWeeny's method for some systems is that it apparently retreats from

(or slows its approach to) a minimum in the energy surface when the

calculated path of steepest descent comes within the vicinity of that

minimum. This would seem to be the nonmonotonic behavior we observed.

As will be shown later, the precise definition of "vicinity" depends

upon the particular system under consideration.

We postulated, therefore, that a combination of the orthodox and

the McWeeny methods would yield convergence. Consequently, we used

27 McWeeny iterations followed by 3 standard diagonalizations. This

procedure gave acceptable convergence and the results in section IV.

With exclusive use of the orthodox method, convergence was

obtained with 15 iterations.

As we will demonstrate shortly, the all-valence-electron systems with which we worked presented fewer difficulties than p-benzoquinone. Because such systems usually present more difficulties than π-electron systems in obtaining convergence, we investigated another π-electron system--calicene--to see whether the above described difficulties were a phenomenon of p-benzoquinone or of π-electron systems in general when the McWeeny method is used.

For calicene we began with the exclusive use of McWeeny's method. After 11 such iterations convergence was obtained monotonically. No change was observed when standard diagonalizations were added. However, nonmonotonic behavior commenced when the technique of averaging the S-matrices was introduced.

To continue our investigation of the McWeeny method a FORTRAN-IV program (14) for all-valence-electron systems was adapted for the McWeeny method (see Appendix). The CNDO approximation (15) was applied to all repulsion integrals. The CNDO/2 parameterization (16) was used to establish the empirical quantities. One-half the charge density and bond order matrix resulting from an extended Hückel calculation was used as a first approximation to $\underset{\sim}{R}$. Slater-type s-, p-, and d-orbitals were used as the basis set.

The all-valence-electron systems with which we worked were the calicene dianion, several configurations of the Cl_2-benzene charge-transfer complex, and a study of selectivity in propylene, nitrobenzene, and m-chloronitrobenzene. While we were able to obtain convergence with exclusive use of the McWeeny method we found that less time was required to do so by using the combination of the

McWeeny and orthodox methods. Utilization of the technique of
averaging the S-matrices actually impeded the obtainment of conver-
gence for all of these systems.

For these systems we did not employ the system of dividing the
total number of iterations into McWeeny-type iterations followed
by a prescribed number of standard diagonalizations. When the
change in the electronic energy between two iterations reached 10^{-3}
a.u. by using the McWeeny method, the orthodox method continued the
calculation until a change of 10^{-6} a.u. was reached. At this point,
convergence was judged to have been obtained.

Because the above procedure did not completely work for the
chlorine-benzene complex, a few additional remarks are necessary.
The binding energy curves for several configurations were constructed
(apparently for the first time) in which the chlorine atoms either
included d-orbitals, excluded d-orbitals or included contracted (less
diffuse) d-orbitals where the Slater exponent had been increased (in
the absolute sense). At short intermolecular distances (2.0 Å and
less) with any inclusion of d-orbitals, any attempt at including stan-
dard diagonalizations with the McWeeny iterations resulted in diver-
gence (see I) before the 10^{-6} a.u. standard for convergence had been
satisfied. Consequently, for such cases we made exclusive use of
the McWeeny method, leading to satisfaction of the 10^{-6} a.u. standard
for convergence.

Towards the end of our work, we found that convergence could be
obtained for the chlorine-benzene complex and the selectivity study
by using the orthodox method with the inclusion of the technique of

averaging of the R-matrices. The results in section IV for the

complex and the selectivity study were obtained by using this method.

At short intermolecular distances, however, the McWeeny method or

the combination of the McWeeny and orthodox methods had to be used.

IV. Results

The purpose of this section is to present and discuss the results obtained by using the McWeeny method and/or the technique of averaging the R-matrices (in the orthodox method) on several π-electron and all-valence-electron systems. While conclusions and recommendations for further investigation of these systems will be given in this section, conclusions and recommendations regarding the methods employed will be presented in the following section.

A. π-electron Systems

1.   p-Benzoquinone

The following data were used as input for the π-electron investigation of p-benzoquinone. (Fig. 2, p. 16). DelW (oxygen) -6.54 e.v. (the negative of the ionization potential of oxygen relative to carbon)

γ_{oo} = 15.23 e.v.

γ_{cc} = 11.13 e.v.   one-center repulsion integrals

$\beta_{c=o}$ = -3.25 e.v.

β_{c-c} = -2.395 e.v.

Output:

E_{π} = -234.290 e.v.

$E_{C.R.}$ = 117.189 e.v.

E_{total} = -117.101 e.v.

Electron density and bond order results, obtained by using McWeeny's method, are given in Fig. 2, p. 16. These results compare favorably with those obtained with the orthodox method.
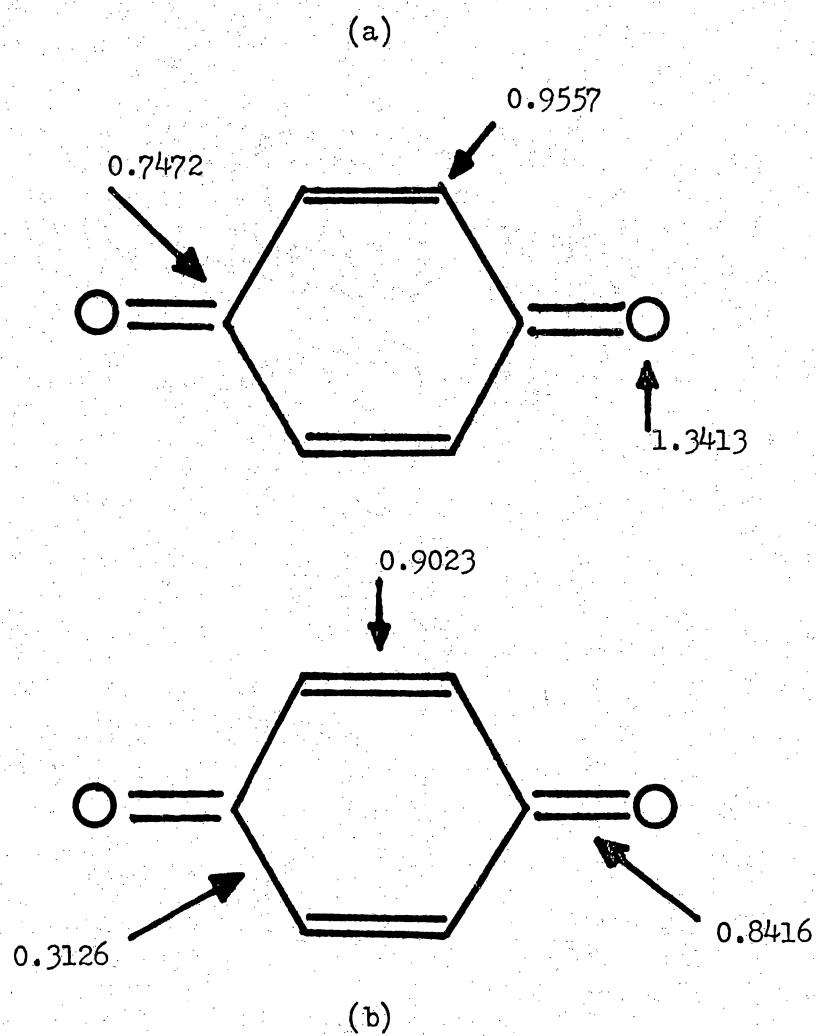
Fig. 2. p-Benzoquinone. Calculated π-electron densities (a) and π-bond orders (b).

2. Calicene

The following data were used as input for the π-electron
investigation of calicene (Fig. 3, p. 18).

β_{cc} = -2.395 e.v.

γ_{cc} = -11.13 e.v.

Geometry: Planar, regular polygons; R_{cc} = 1.395 Å

    Output:

E_{π} = -212.780 e.v.

$E_{C.R.}$ = 110.840 e.v.

E_{total} = -101.940 e.v.

   Analysis: Unsubstituted calicene has not as yet been prepared
in the laboratory. This is at least partially understandable when
one realizes that calicene has 8 π-electrons (antiaromatic, according
to Hückel's 4n+2 rule).

An alternative view of calicene is obtained when one considers
the system as two joined rings. If one considers the 1,2 bond as
polarized with both of its π-electrons in the cyclopentadiene ring,
the result is a cyclopentadienyl anion and a cyclopropenyl cation.
Both of these systems are aromatic according to Hückel's rule. In
this picture an unstable 8 π-electron system becomes the combination
of two stable π-electron systems (6 and 2 π-electrons, respectively).

To test this proposition, one should consider the π-electron
distribution and the bond orders of Fig. 3, p.18. The 1,2 bond order
is only 0.6145 (it should be closer to 0.0) which indicates only
slight polarization of the bond. Also, the net charge in each ring
is only .5687. A net charge of 1.0 should have been obtained in

(a)

(b)
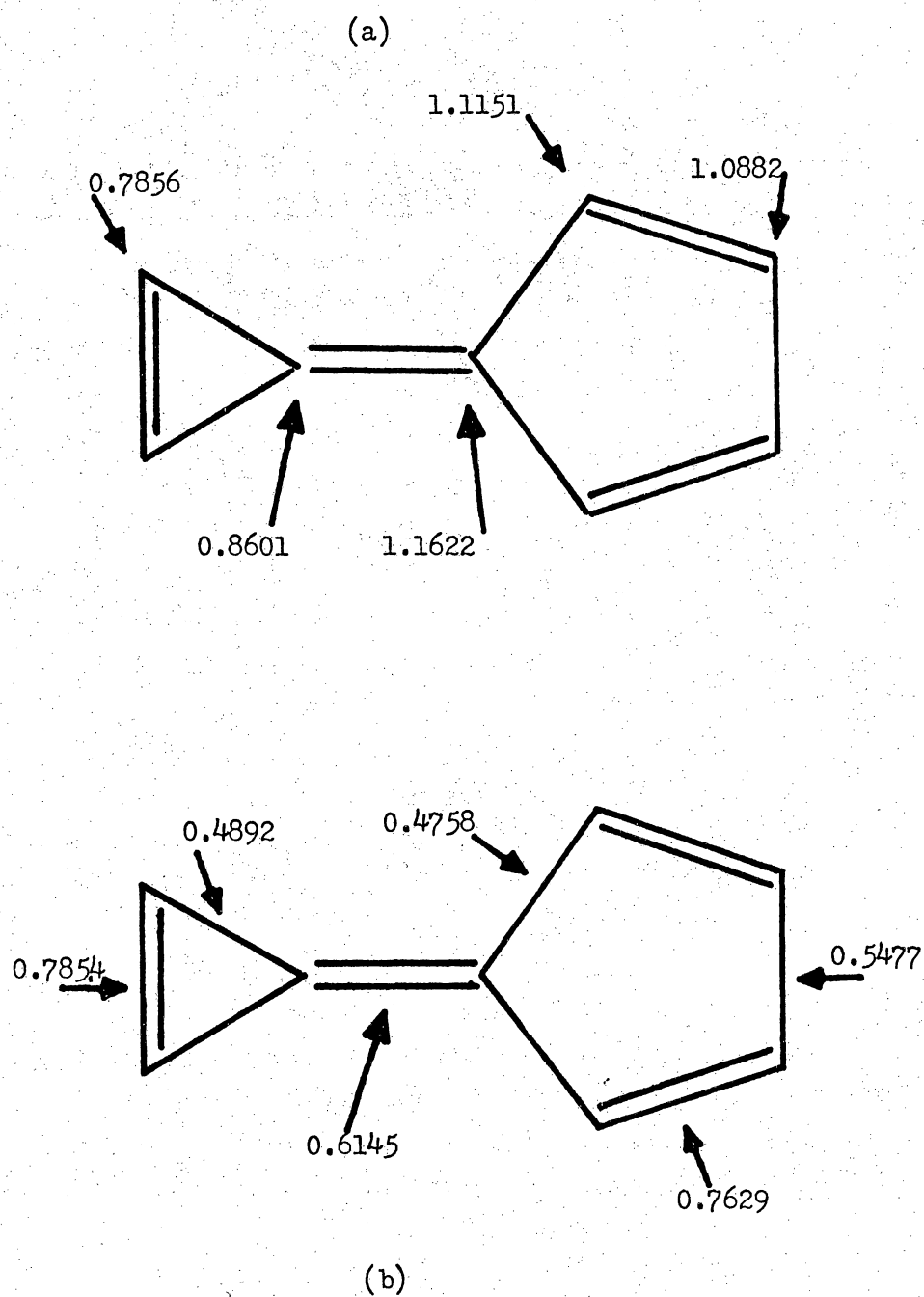
Fig. 3. Calicene. Calculated π-electron densities (a)
and π-bond orders (b)

order for the above-stated aromatic condition to be present. Appar-
ently, based upon these calculations at least, the 8 π-electron
picture of calicene is the more accurate picture and is one
possible reason for the lack of preparation of calicene.

B. All-valence-electron Systems

1. Calicene Dianion

The results for the calicene dianion (planar; MINDO parameters) are given in Fig. 4, p. 21. These results were obtained with the McWeeny method; earlier attempts to make this calculation with the orthodox method resulted in divergence.

$E_{Binding}$ = -2.55128 a. u. = 1603.0202 kal./mole.
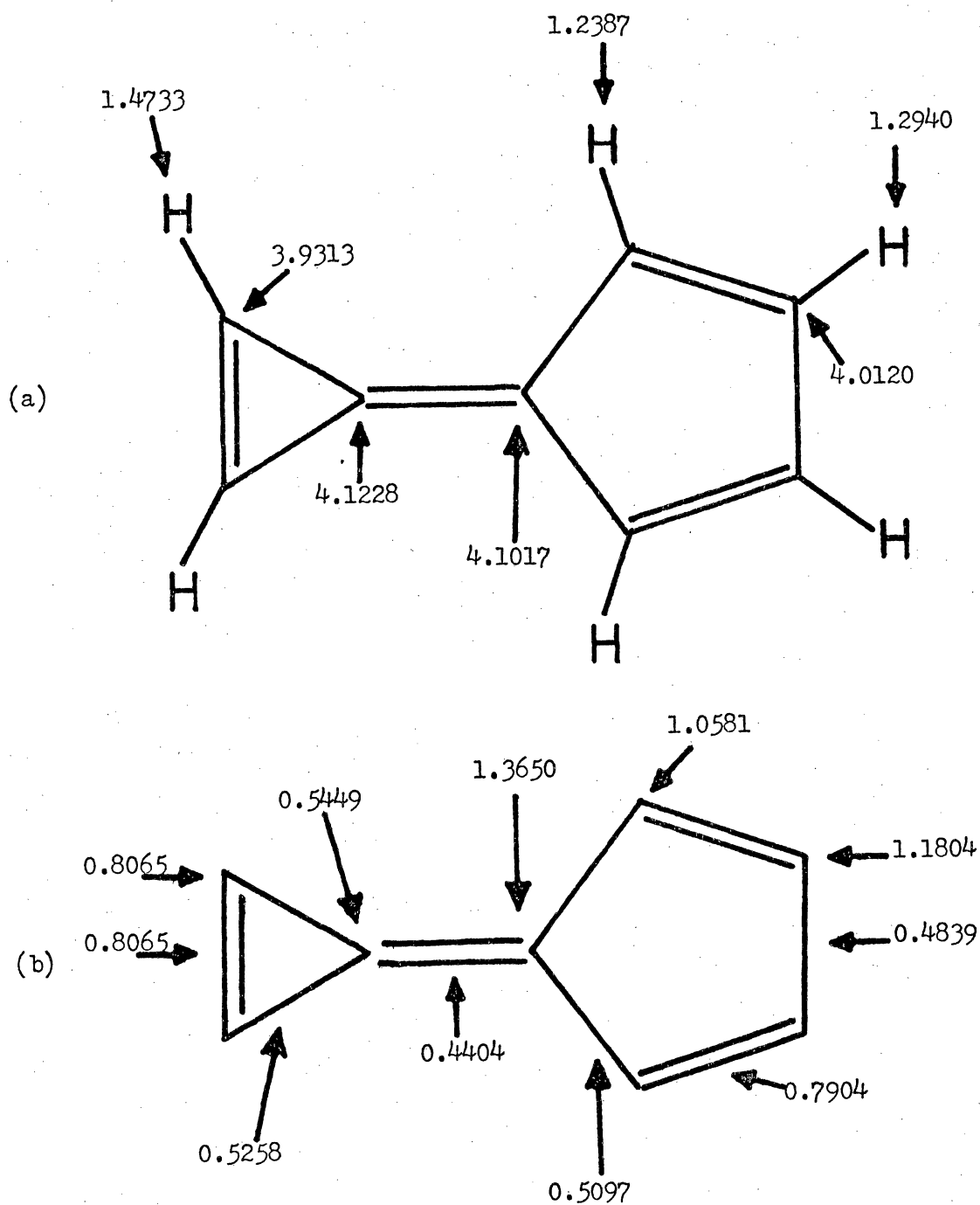
Fig. 4. Calicene dianion. (a) Total valence electron densities.
(b) π-electron densitites and π-bond orders.

2. The Cl_2-Benzene Charge-transfer Complex

Intuitively, chemists and physicists would not predict any form of intermolecular bonding between benzene (or its homologues) with its highly stable aromatic π-electron system and a halogen molecule with its fully occupied s- and p-shells. While benzene does undergo substitution by halogens (in the presence of a Lewis acid), addition reactions are not observed to occur (except, for example, under conditions of high temperature and pressure in the case of hydrogenation). Nonetheless, while bonding between benzene and a halogen molecule would not be expected, it is observed spectrophotometrically as what has come to be called a "charge-transfer complex" (17).

Because of the experimental observation of the charge-transfer complex, one would be justified in postulating the feasibility of calculating the binding energy and other physical properties of these systems through theoretical methods. In the past, various techniques of perturbation theory have been utilized (18); however, all attempts at employing approximate SCFMO theory have resulted in divergence. With the technique of averaging the R-matrices in the orthodox method (see III), we are able to obtain convergence at most intermolecular distances; however, at short distances (2.0 Å and less) divergence still occurred. With the advent of the McWeeny method, even these converged. Consequently, calculation of complete binding energy curves became feasible.

We constructed binding energy curves for several configurations of the complex between benzene and Cl_2. The intermolecular distances (R) are measured from the center of the benzene ring to Cl_1 (the

nearest chlorine atom). $E_B(R)$ is the binding energy relative to the isolated atoms, and $E_{I.M.} = E_B(R) - E_B(\infty)$ is the binding energy relative to the isolated molecules. In these results $E_B(\infty)$ is taken to be the binding energy at the farthest distance calculated. The quantities $q_{Cl_{(1)}}$ and $q_{Cl_{(2)}}$ are the charges found to be present on chlorine atoms #1 and #2, respectively. $q_{C.T.} = q_{Cl_{(1)}} + q_{Cl_{(2)}}$ is the amount of charge transferred from one molecule to the other in the complex.

The experimental value of the equilibrium R, as measured from a crystal (which has exclusively an axial configuration), is 3.28 Å (19). The equilibrium value for $E_{I.M.}$ of the axial configuration is -1.1 kcal/mole. (20). (While the crystalline form of this complex is in the axial configuration, it is believed that the complex in solution exists in a variety of configurations.)

From Tables 1 and 2, pp. 25 and 27, and Figs. 5 and 6, pp. 26 and 28, it can be seen that the binding energy wells (which indicate the equilibrium values for $E_{I.M.}$ and R) are far too deep when compared to experimental values when d-orbitals are included on the chlorine atoms. Because of these highly unrealistic results, dipole moments and charge distributions for these systems were not considered.

When contracted d-orbitals (the absolute value of the orbital exponent was increased) were used, sufficiently unsatisfactory results (the binding energy wells were still much too deep) were obtained to warrant no further consideration of these systems. Consequently, these results have not been included here.

When the d-orbitals were completely eliminated from the chlorine atoms (21), much more satisfactory results were obtained, as can be seen from Tables 3, 4, and 5, pp. 31, 35, and 39, and Fig. 8, 10, and 12, pp. 32, 36, and 40. Each of the configurations (axial, planar, and resting) will be discussed individually.

At first glance it might be surprising that better results were obtained when the smaller basis set was used. The reverse is certainly expected when _ab_ _initio_ calculations are performed. However, this frequently happens in semi-empirical treatments.

Table 1. Axial Configuration of the Cl_2-Benzene Complex
(d-orbitals on the chlorine)

R_{o-Cl_1} Å	$E_B(R)$ kcal/mol	$E_{I.M.}$ kcal/mol
1.5	-6926.59	-765.92
2.0	-6504.36	-406.52
2.5	-6169.47	-71.62
3.0	-6251.78	-153.93
3.5	-6163.19	-65.34
4.0	-6122.35	-24.50
4.5	-6106.01	-8.16
5.0	-6100.35	-2.51
5.5	-6098.47	-.62
6.0	-6097.85	0.0

$E_{I.M.}$ curve has no minimum

Fig. 5. Binding Energy ($E_{I.M.}$)
Curve for the Axial
Configuration of the Cl_2-Benzene
Complex (d-orbitals on Cl_2).

Table 2 . Planar Configuration of the Cl_2-Benzene Complex
(d-orbitals on the chlorine)

R_{o-Cl_1} Å	$E_B(R)$ kcal/mol	$E_{I.M.}$ kcal/mol
1.5	-550.40	5547.43
2.0	-4862.56	1235.27
2.25	-5955.84	142.00
2.5	-6432.74	-334.89
2.75*	-6558.40	-460.55
3.0	-6524.47	-426.62
3.5	-6334.09	-236.24
4.0	-6158.16	-60.31
4.5	-6189.58	-91.73
5.0	-6136.80	-38.95
5.5	-6112.29	-14.45
6.0	-6102.87	-5.02
6.5	-6097.84	0.0

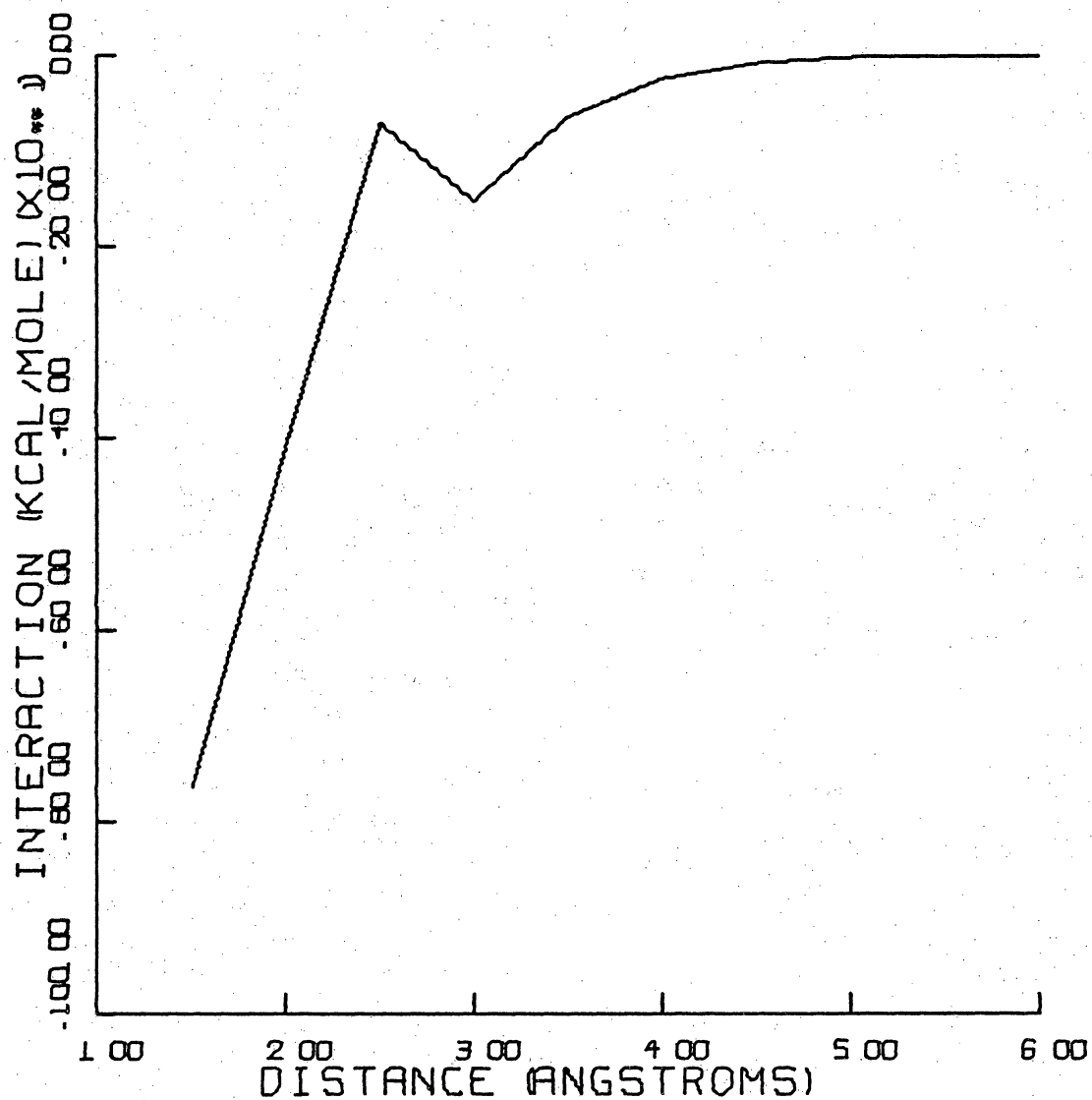* indicates configuration at minimum $E_{I.M.}$

Fig. 6. Binding Energy ($E_{I.M.}$)
Curve for the Planar
Configuration of the Cl_2-Benzene
Complex (d-orbitals on Cl_2).

a. Axial Configuration (Fig. 7)

Table 3, p. 31, and Fig. 8, p. 32 show a calculated equilibrium

R and $E_{I.M.}$ of 2.0 Å and 10.2 kcal/mole., respectively. While these

results indicate stronger bonding than is revealed experimentally,

$E_{I.M.}$ is only one order of magnitude removed from the experimental

value (-1.1 kcal/mole.) which indicates the procedure is in the

correct direction for eventually obtaining theoretically favorable

results.

The charge distribution data in Table 3, p. 31, shows some very

interesting results. In the region of 1.5 Å-4.0 Å the values for

$q_{C.T.}$ indicate that charge is transferred from the benzene to the

chlorine molecule. Since the binding energy minimum is located in

this region, it can be concluded that at least part of the bonding of

this complex in this configuration is Coulombic in nature. Beyond

4.0 Å no charge is transferred; however, polarization of the chlorine

molecule is observed since the chlorine atoms are charged. It is

interesting to notice that the direction of polarization is reversed

at 4.0 Å and beyond. The polarization is believed to be the result

of the presence of a quadrupole moment for the π-electron system of

benzene which creates an electric field which polarizes the chlorine

molecule. Because this polarization is observed in the region of the

binding energy minimum, it, together with the above-described Coulombic

force, are at least components of the bonding in this configuration of

the complex.

We obtained an equilibrium dipole moment of 1.7 D. While no

experimental values for this complex are available, other halogen-

benzene complexes have dipole moments in the region of 1.0 D (22).

Fig. 7. Axial Configuration of the Cl_2-Benzene Complex where the Cl_2 molecule bond lies along the C_6 axis of benzene.

Table 3. Axial Configuration of the Cl_2-Benzene Complex
(no d-orbitals on chlorine)

R_{o-Cl_1} Å	$E_B(R)$ kcal/mol	D	$E_{I.M.}$ kcal/mol	q_{Cl_1}	q_{Cl_2}	$q_{C.T.}$
1.5	-5268.84	3.2	81.24	+.1051	-.2013	-.0962
2.0*	-5360.32	1.7	-10.24	+.0519	-.1070	-.0551
2.5	-5359.56	0.6	-9.48	+.0175	-.0378	-.0203
3.0	-5353.09	0.2	-3.01	+.0039	-.0093	-.0054
3.5	-5350.77	0.03	-.69	+.0003	-.0015	-.0012
4.0	-5350.20	0.0	-.12	-.0003	+.0001	-.0002
4.5	-5350.14	0.0	-.06	-.0003	+.0003	0.0
5.0	-5350.08	0.0	0.0	-.0002	+.0002	0.0
5.5	-5350.08	0.0	0.0	-.0002	+.0002	0.0
6.0	-5350.08	0.0	0.0	-.0001	+.0001	0.0

* indicates configuration at minimum $E_{I.M.}$
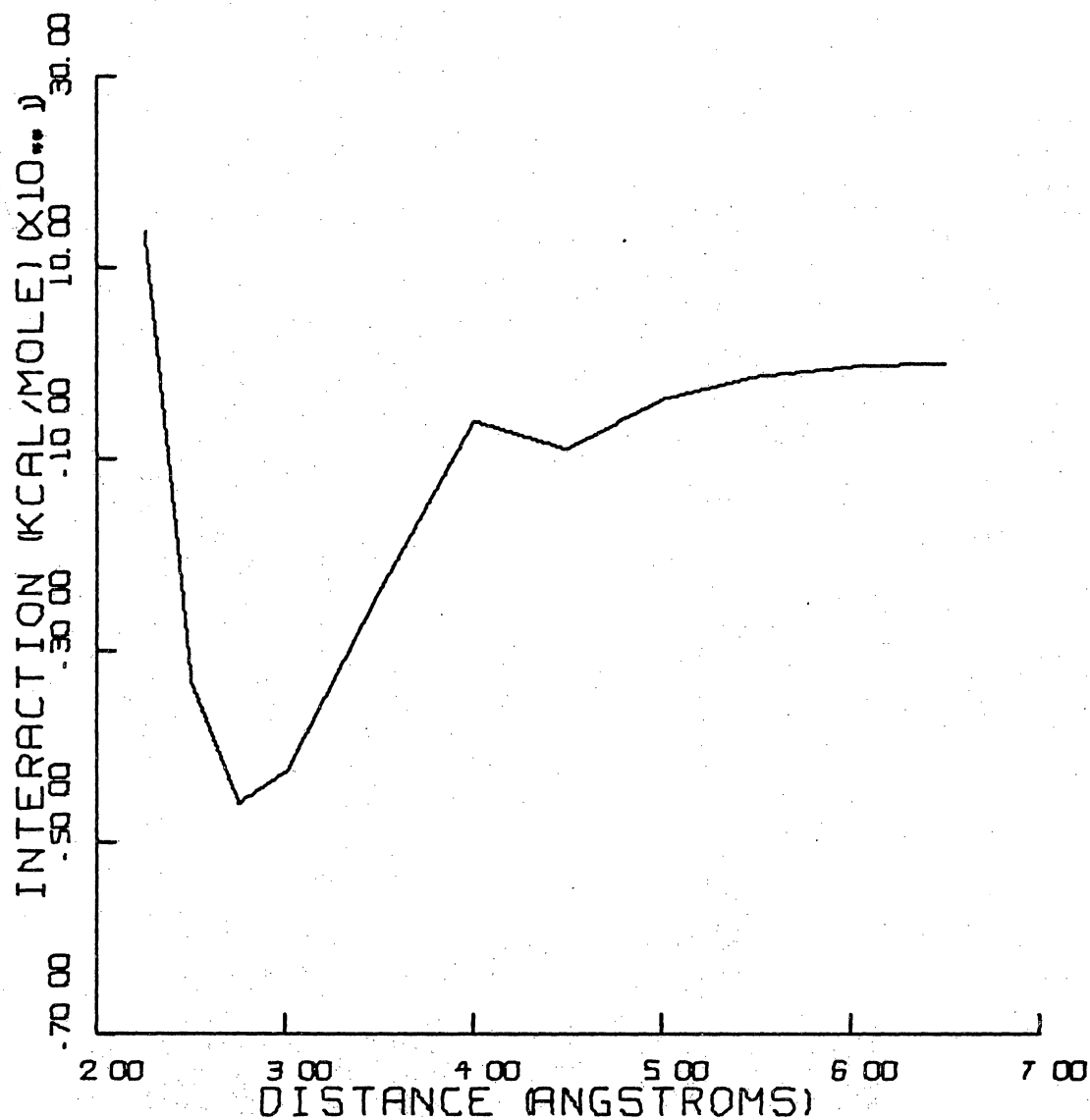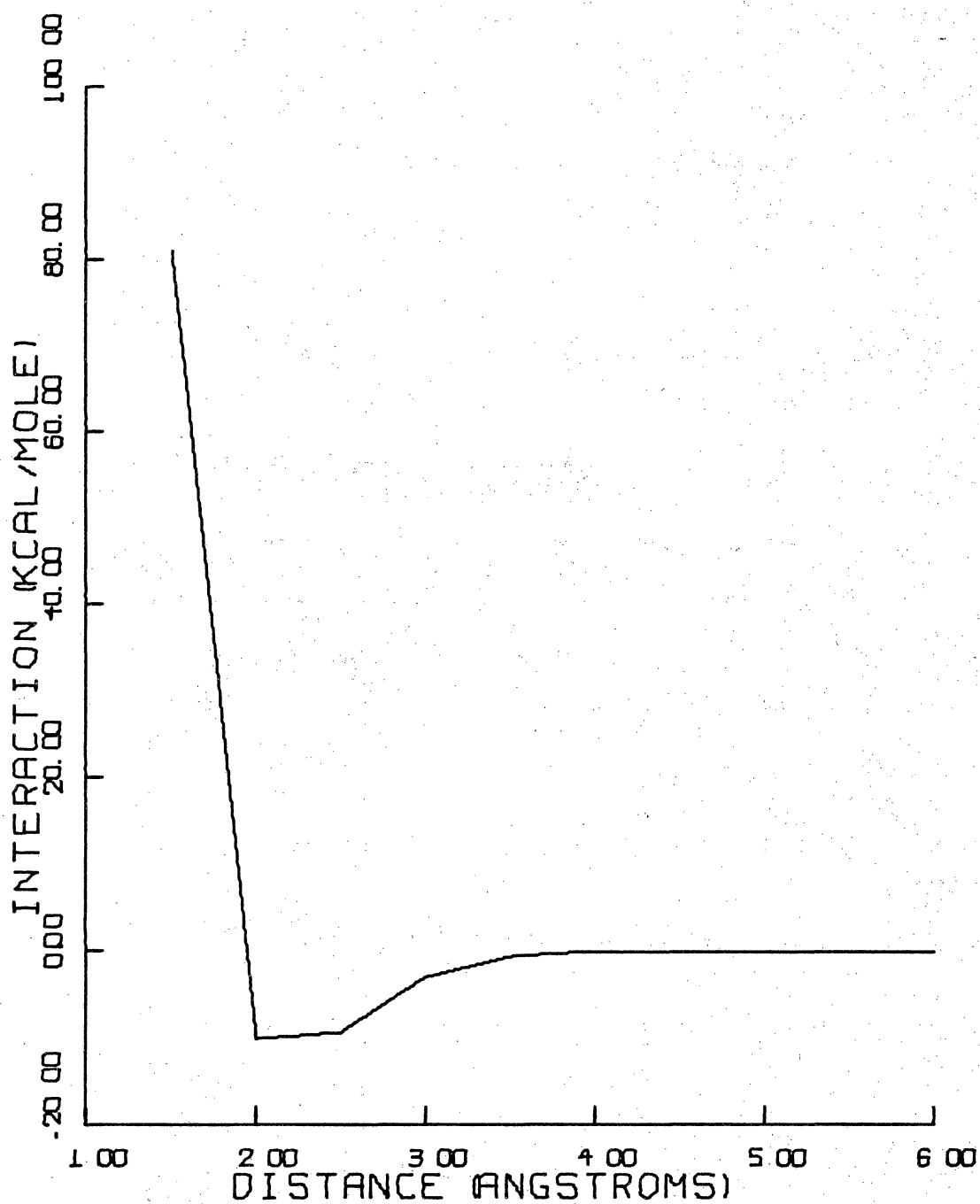
Fig. 8. Binding Energy ($E_{I.M.}$) Curve for the Axial
Configuration of the Cl_2-Benzene Complex (no d-orbitals
on Cl_2).

b. Planar Configuration (Fig. 9)

The results for the planar configuration are given in Table 4, p. 35, and Figure 17, p. 53.

The longer equilibrium intermolecular bond length for the planar configuration over that for the axial configuration (4.0 Å instead of 2.0 Å) and the consequent lower binding energy for the planar configuration (-7.10 kcal/mole. instead of -10.24 ckal/mole.) are presumably due to the steric hindrance of the benzene hydrogens. Also, because the chlorine molecule axis (see Fig. 9, p. 34) is in the nodal plane of the π-systems, it is reasonable to conclude that there is less interaction between the respective electron systems.

These results are highly theoretical because they cannot be confirmed experimentally. While x-ray analysis confirms the exclusive presence of the axial configuration in the crystalline form of this complex, it has been only postulated that the planar configuration (and others) are present in the solution form which is not amenable to such analysis (23).

The charge distribution in Table 4, p. 35, shows charge-transfer in the region of 2.0 Å - 5.5 Å. (The transfer of charge from the Cl_2 molecule to benzene at 2.0 Å is most probably due to this being a totally physically unrealistic intermolecular separation since $E_{I.M.}$ is positive, indicating repulsion.) Beyond 5.5 Å only polarization is seen. No reverse in the direction is seen as was observed for the axial configuration. Because both charge-transfer and polarization are observed in the region of the minimum of the $E_{I.M.}$ curve, both components are responsible for the intermolecular bonding in this configuration (if it exists at all).
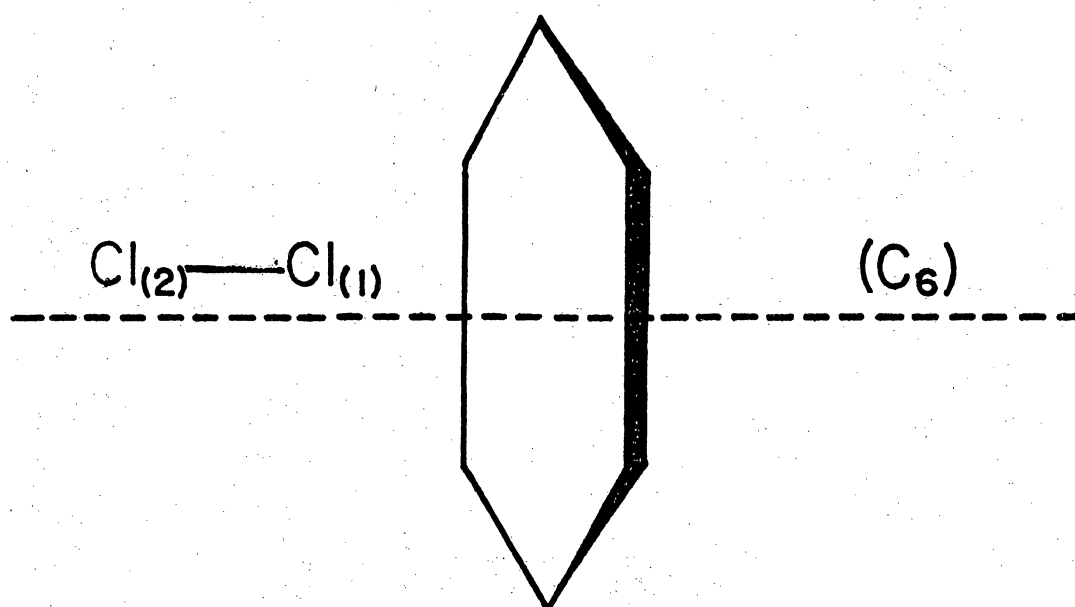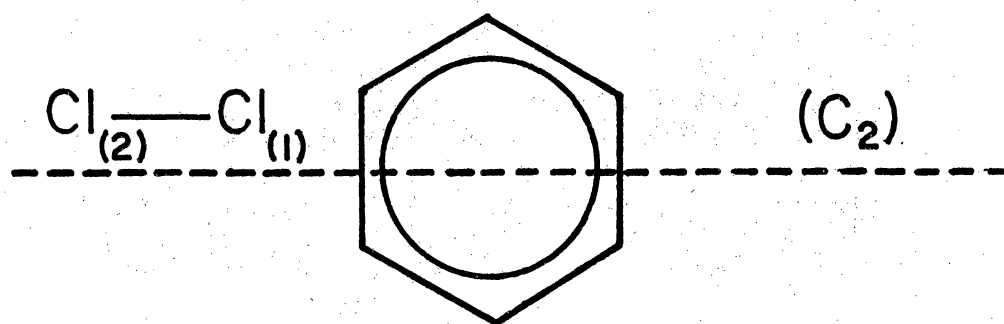
Fig. 9. Planar Configuration of the Cl_2-Benzene Complex where the Cl_2 molecule bond lies along a C_2 axis of benzene.

Table 4 . Planar Configuration of the Cl_2-Benzene Complex (no d-orbitals on chlorine).

| R_{o-Cl_1} Å	$E_B(R)$ kcal/mol	D	$E_{I.M.}$ kcal/mol	q_{Cl_1}	q_{Cl_2}	$q_{C.T.}$
2.0	-2741.54	2.1	2608.53	+.5528	-.2720	+.2808
2.5	-4729.30	4.2	620.78	+.1895	-.2868	-.0973
3.0	-5257.53	3.2	92.55	+.1027	-.2030	-.1003
3.5	-5352.97	1.5	-2.89	+.0484	-.0935	-.0451
4.0*	-5357.18	0.5	-7.10	+.0164	-.0306	-.0142
4.5	-5352.72	0.1	-2.63	+.0043	-.0076	-.0033
5.0	-5350.77	0.03	-.69	+.0010	-.0016	-.0006
5.5	-5350.20	0.01	-.12	+.0003	-.0004	-.0001
6.0	-5350.14	0.0	-.06	+.0001	-.0001	0.0
6.5	-5350.08	0.0	0.0	+.0001	-.0001	0.0

* indicates configuration at minimum $E_{I.M.}$

Fig. 10. Binding Energy ($E_{I.M.}$) Curve for the Planar
Configuration of the Cl_2-Benzene Complex (no d-orbitals
on Cl_2).

c. Resting Configuration (Fig. 11)

The results for the resting configuration are given in Table 5, p.39 , and Fig. 12, p.40 . The same remarks regarding the validity of the results for the planar configuration also hold here since the resting configuration too has not been observed experimentally.

Nevertheless, the intermolecular distance is found to be 3.0 $\overset{o}{A}$ and $E_{I.M.}$ is -.44 kcal/mole. This configuration has been calculated to be repulsive by the perturbation theory, and while this is not found to be the case according to the molecular orbital theory it is understandable why the value for $E_{I.M.}$ is so small.

The charge distribution in Table 5, p. 39, is quite different from those for the axial and planar configurations, since $q_{Cl_{(1)}} = q_{Cl_{(2)}}$. There is no polarization of the chlorine molecule, which is the result of symmetry of the system. From these results only charge-transfer is involved in the intermolecular bonding of the complex. Also, it is interesting to note that most of this charge-transfer is from the chlorine molecule to benzene instead of from benzene to Cl_2 as has been the case with the other configurations.
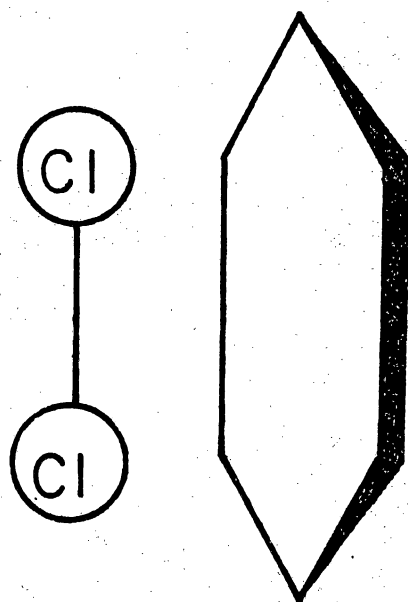
Fig. 11. Resting Configuration of the Cl_2-Benzene Complex

Table 5. Resting Configuration of the Cl_2-Benzene Complex
(no d-orbitals on chlorine)[2]

R_{o-Cl_1} Å	$E_B(R)$ kcal/mol	D	$E_{I.M.}$ kcal/mol	$q_{Cl_1} = q_{Cl_2}$	$q_{C.T.}$
1.0	-2656.59	4.0	2692.85	+.1817	+.3634
1.5	-5043.96	0.5	306.11	-.0286	-.0572
2.0	-5318.60	0.7	31.47	-.0072	-.0144
2.5	-5349.13	0.3	.94	+.0060	+.0120
3.0*	-5350.52	0.1	-.43	+.0009	+.0018
3.5	-5350.20	0.0	-.12	+.0001	+.0002
4.0	-5350.14	0.0	-.06	0.0	0.0
4.5	-5350.08	0.0	0.0	0.0	0.0
5.0	-5350.08	0.0	0.0	0.0	0.0
5.5	-5350.08	0.0	0.0	0.0	0.0
6.0	-5350.08	0.0	0.0	0.0	0.0
6.5	-5350.08	0.0	0.0	0.0	0.0

* indicates configuration at minimum $E_{I.M.}$
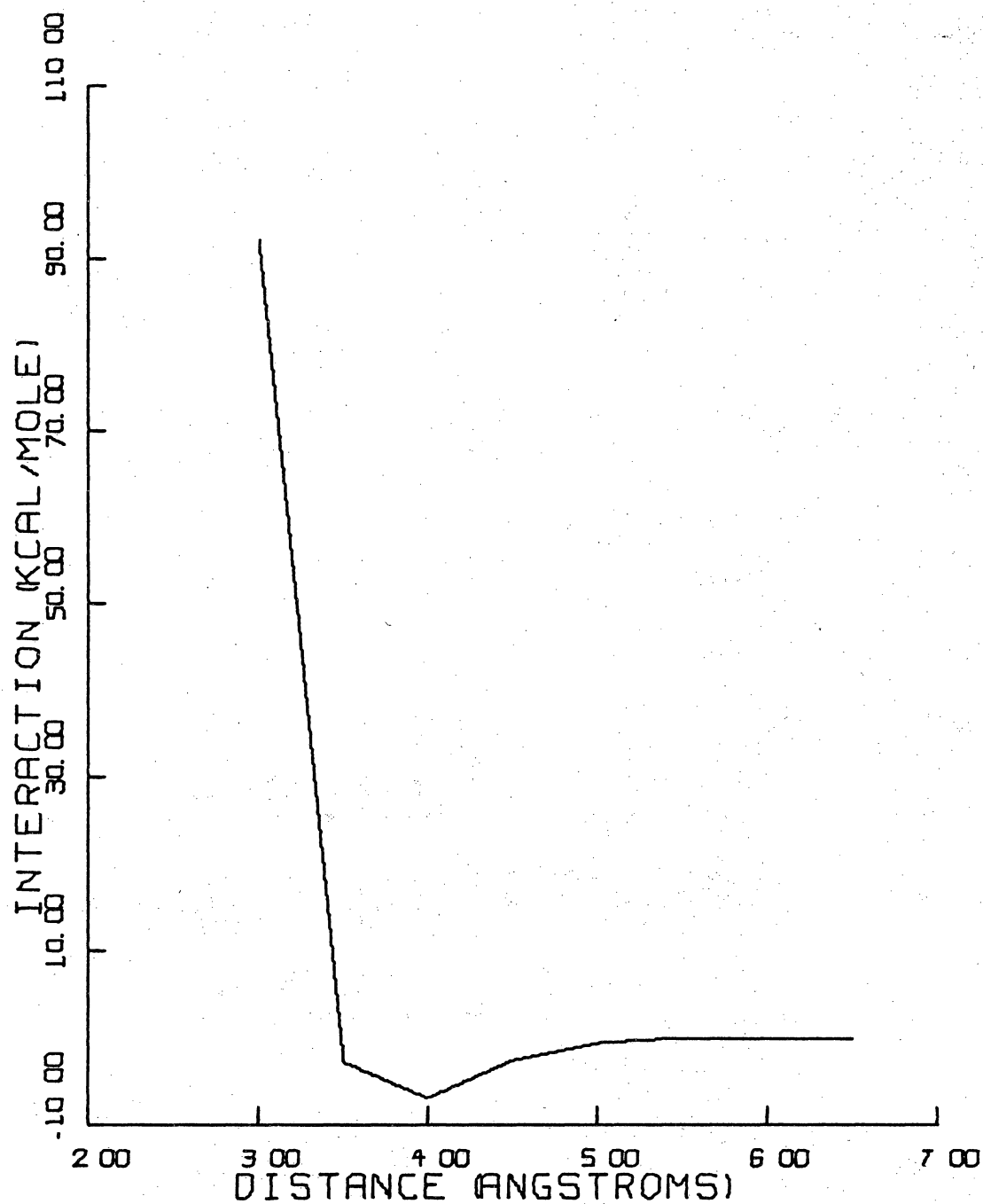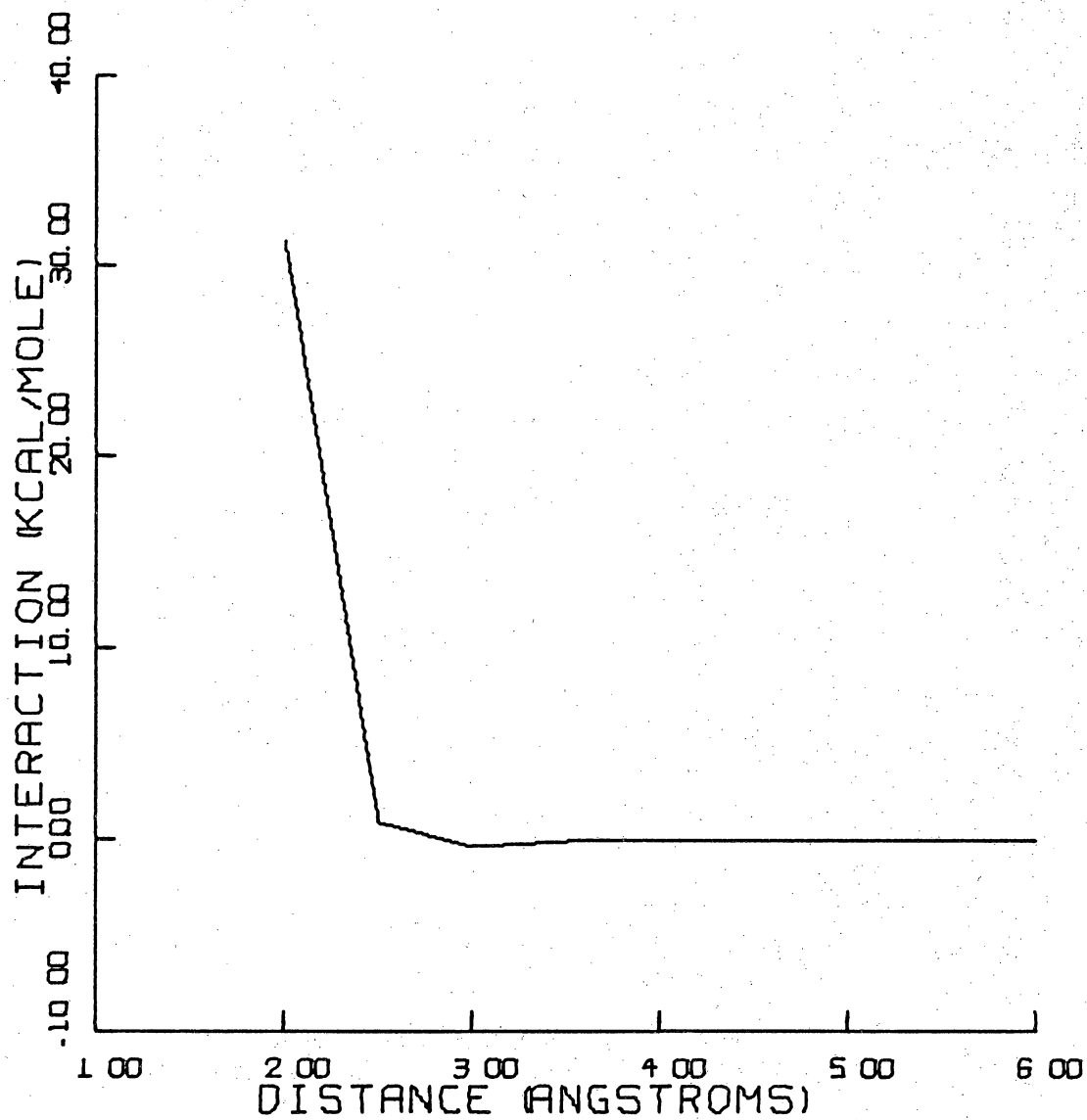
Fig. 12. Binding Energy ($E_{I.M.}$) Curve for the Resting
Configuration of the Cl_2-Benzene Complex (no d-orbitals
on Cl_2).

d. Conclusion

The elimination of d-orbitals on the chlorine atoms increases the accuracy of the equilibrium $E_{I.M.}$ by 1-2 orders of magnitude. Because these complexes are so unusual, it may be justified to increase the absolute value of the exponential of the s- and/or p-orbitals for the chlorine and/or benzene. This would have the effect of creating less diffuse orbitals and thus decreasing the involvement of the altered orbitals in the bonding of the complex which should give a more realistic equilibrium $E_{I.M.}$.

The charge distributions for the axial and planar configurations show a combination of charge-transfer and polarization in the intermolecular bonding of the complex while no polarization is revealed for the resting configuration.

These results are the first to be obtained for these complexes by use of the SCFMO theory. While we only examined three configurations, there are many more possible ones; and they should be investigated in order to examine the possible configurations of this complex in solution. Also, other complexes formed from other halogens and benzene (and its derivatives) should be investigated.

C. Positional Selectivity in Chemical Reactions

Chemists have long sought quantitative as well as qualitative
means by which to determine and rationalize selectivity in a series
of related chemical reactions. The linear free energy quantities of
Hammett and others (24) and the localization energy of G.W. Wheland
(25) are examples of the quantitative methods while the theories of
resonance and hyperconjugation are examples of the qualitative methods.
All such (experimental) methods are the attempts of the chemist to
reduce "related" reactions to the fewest differentiating factors and
therefore affording him an efficient but simple and systematic means
of predicting selectivity.

Moreover, the theoretician attempts to deal with this problem
by "performing reactions by computer" with its attendant flexibilities
and uncertainties. By arranging the molecules and other participating
species in a desired configuration (actually the method involves the
arranging of the atoms which make up the overall configuration) and
permitting or excluding orbital interactions, he attempts to determine
selectivity from the relative binding energies of approximations to the
transition state. With an appropriate approximate SCFMO method, the
binding energies resulting from attack at the possible sites of the
substrate are calculated. The binding energy with the highest absolute
value is judged to correspond to the site of the highest percentage of
attack, etc. That is, the order of the absolute values of the binding
energies should correlate directly with the order in the isomer distri-
bution.

Using the CNDO/2 approximation we sought to utilize the above method to study positional selectivity. The systems which we studied are the protonation (addition of Brønsted acids) of propylene and the chlorination of nitrobenzene and m-chloronitrobenzene.

1. Addition of Brønsted Acids to Propylene

The first example of studying selectivity through results obtained from the CNDO/2 approximation is the protonation of (addition of Brønsted acids to) propylene. The mechanism for such reactions is shown in Fig. 13, p. 45. The rate-determining step is the formation of carbonium ion I or II (26). Also, the formation of a carbonium ion would be expected to control the isomer distribution of the product based upon this mechanism.

Our task was to predict the qualitative selectivity in this reaction through the electron distribution of propylene and the binding energies of the respective carbonium ions. One would expect the electrophilic proton to attack the carbon position of higher electron density the most frequently. Also, the resulting carbonium ion should have the higher absolute binding energy and therefore, be the more stable. The isomer distribution should, therfore, reflect this situation by having the more abundant isomer, resulting from the more stable carbonium ion. If any of the alternative isomer is formed, it would, of course, come from the less stable carbonium ion.

The electron distribution of propylene (27) is shown in Fig. 14, p. 46 . The proton would be expected to attack most frequently carbon position #1 which experimentally is what happens (see Fig. 14, p. 46).

The binding energies and the electron distributions of the carbonium ions are shown in Fig. 15, p. 47 . The carbonium ion of higher absolute binding energy does indeed result, also, in the more abundant isomer. The electron distribution of these ions shows that the positive charge is delocalized more in the more stable ion, thus accounting for the higher stability (as predicted by resonance theory).
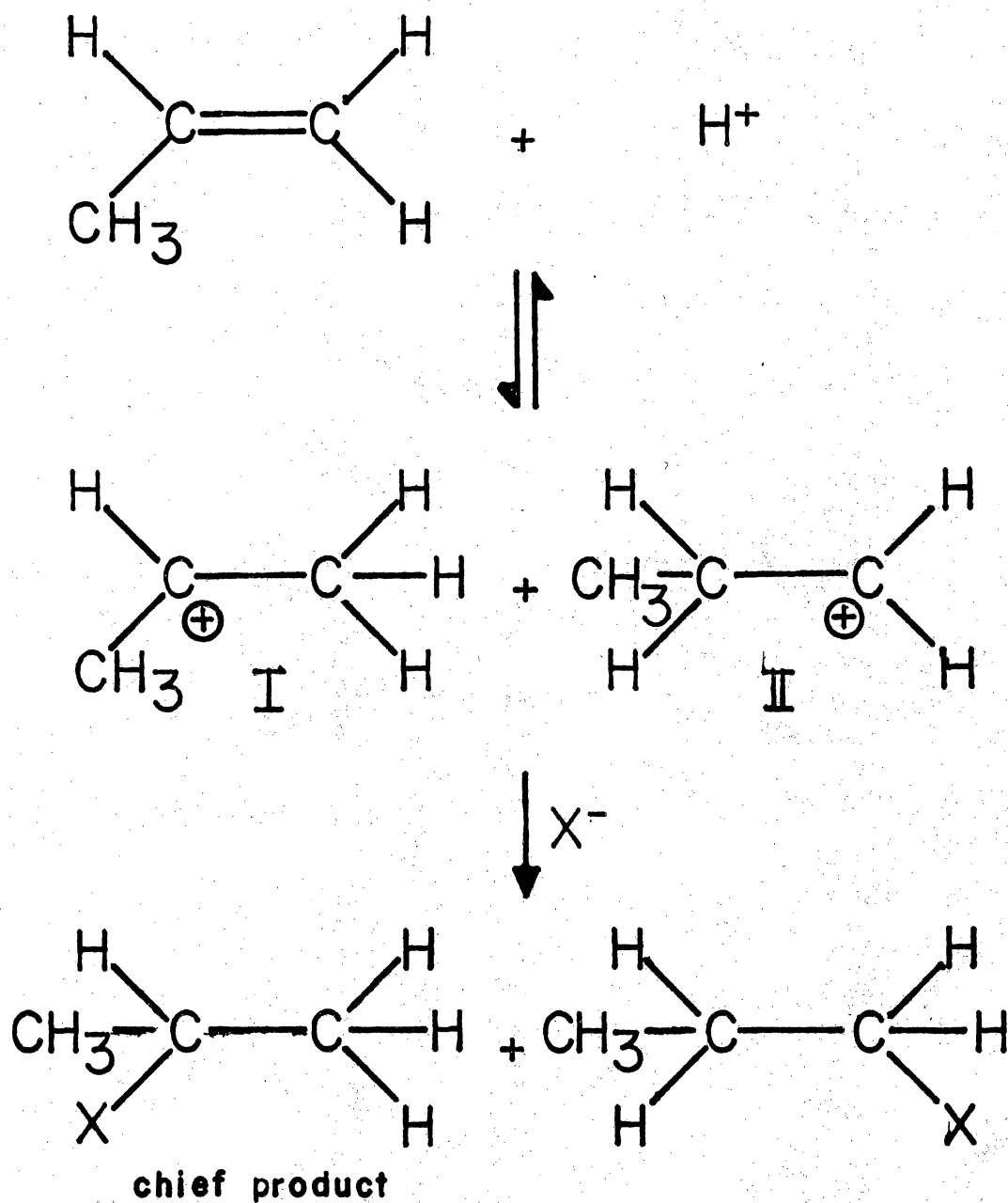
Fig. 13. Mechanism of the Addition of Brønsted Acids to Propylene. (In the addition of HI to propylene, the exclusive product is isopropyl iodide.)
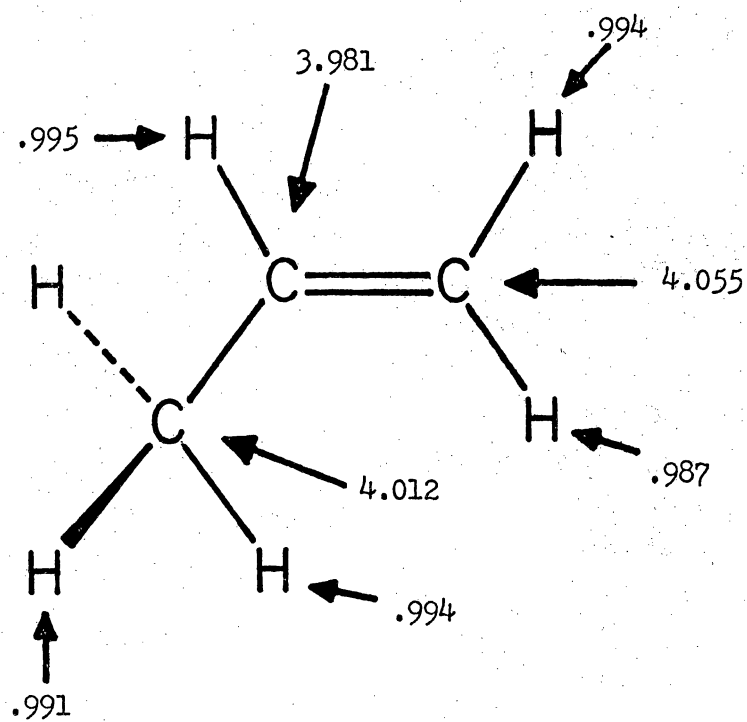
Fig. 14. All-valence-electron Distribution of Propylene.
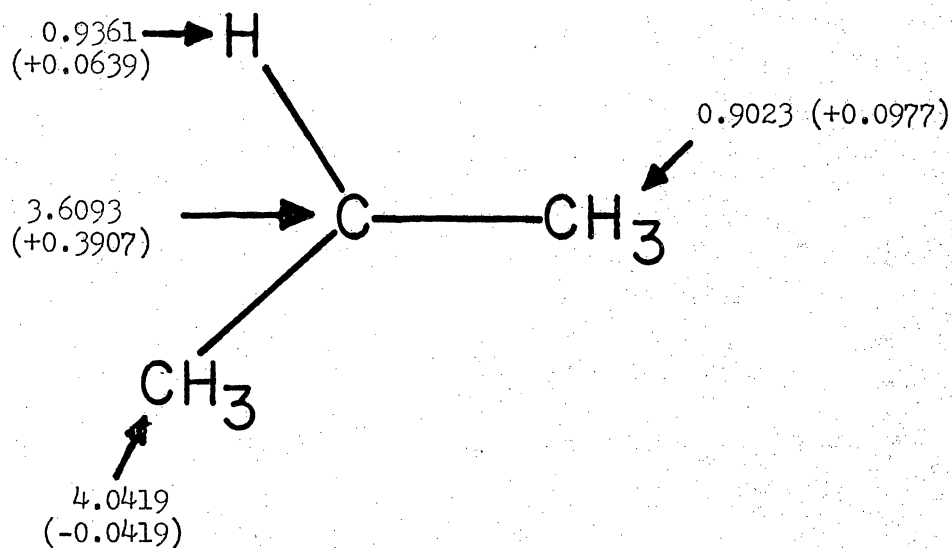
I. $E_{binding}$ = -2029.47 kcal/mol.
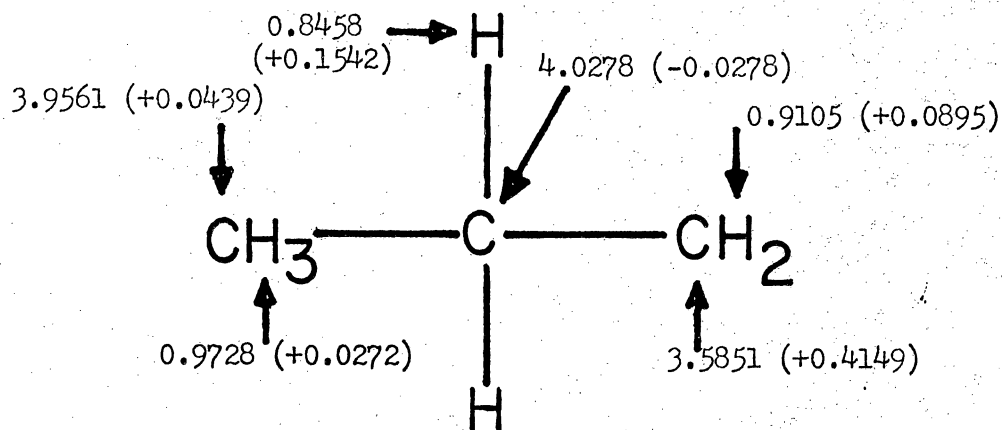
II. $E_{binding}$ = -1989.20 kcal/mol.

Fig. 15. All-valence electron densities and net charges (in parenthesis) calculated for the propyl cations I and II. Average quantities are shown for the H atoms in CH_3 and terminal CH_2 groups.

Thus, studying the CNDO/2 electron distribution of propylene
or the binding energies of the respective carbonium ions leads to
a correct predicition of selectivity in the addition of Brønsted
acids to propylene.

2. The Chlorination of Nitrobenzene

To follow are our attempts to study positional selectivity in the chlorination of nitrobenzene by means of the CNDO/2 approximation. In the course of our studies, we were confronted by some apparent contradictions and inconsistencies, the resolution of which was not completely realized. We will, however, present some recommendations for further investigation which may help to clarify the situation.

One of the accepted mechanisms for the chlorination of nitrobenzene (electrophilic aromatic substitution) is shown in Fig. 16, p. 50. (A more sophisticated alternative will be presented later.) From kinetics studies, the formation of the chloronitrobenzenium ion is the rate-determining step (28). Consequently, it is also this step which determines the isomer distribution of the product.

Based upon this mechanism the Hammond postulate (29) states that the transition state (of the rate-determining step) is generally more similar to either the reactant (substrate) or product (intermediate), whichever is at the higher energy. Consequently, whether the chlorination of nitrobenzene is exothermic or endothermic should suggest whether we should primarily be considering the nitrobenzene substrate or chloronitrobenzenium ion intermediate, respectively, in studying positional selectivity. Unfortunately, we were unable to locate the necessary thermodynamic data with which to make such a determination. Therefore, we considered both possibilities in our calculations, hoping to find only one consistent with the experimental results.
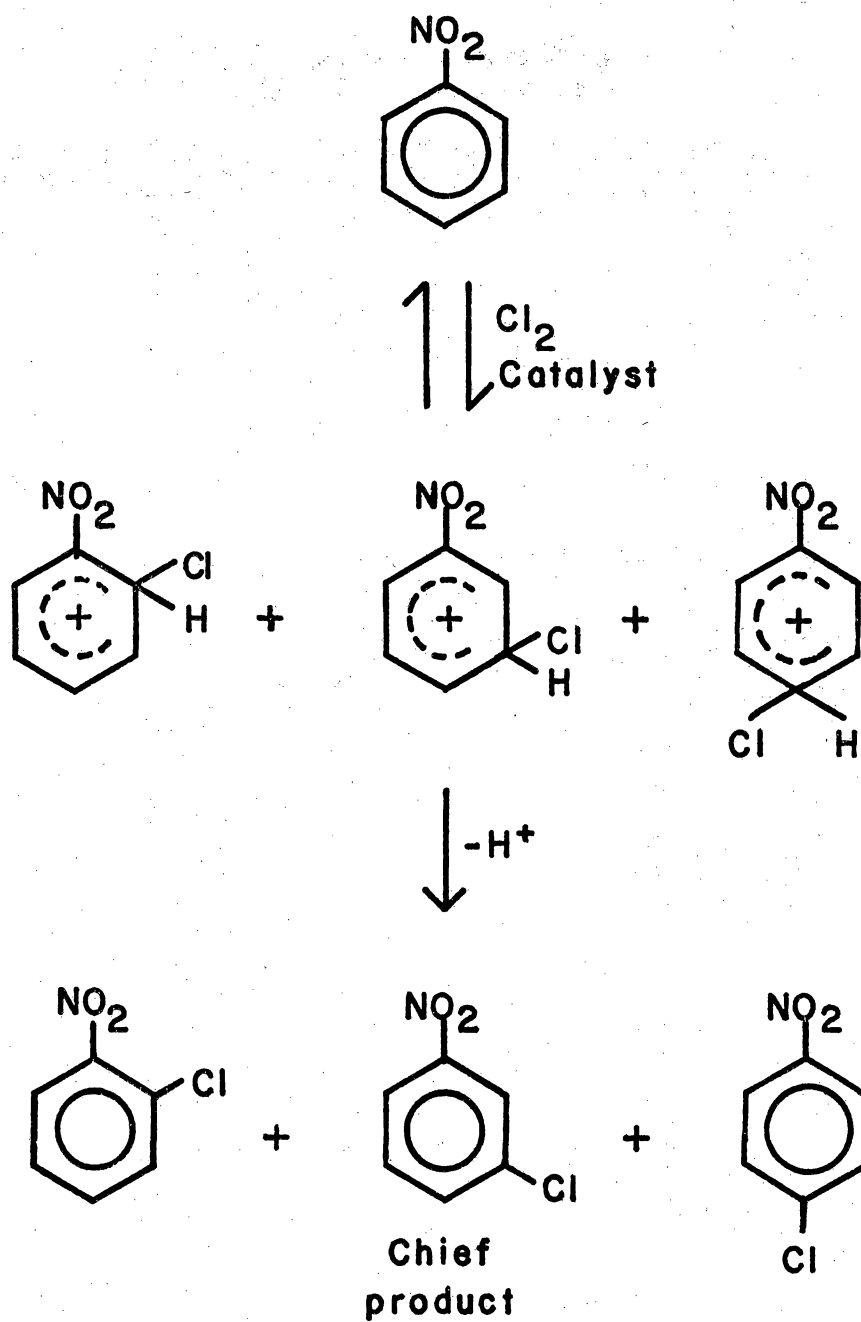
Fig. 16. Mechanism of the Chlorination of Nitrobenzene.

When a CNDO/2 calculation is performed for nitrobenzene, the electron distribution of Fig. 17, p. 53 is obtained. (While the geometric data for nitrobenzene in the liquid phase is desirable, such data are not available. Therefore, geometric data for the solid phase was used which revealed a planar configuration for nitrobenzene (30).) It is reasonable to expect the (electron-poor) chloronium ion electrophile to attack (to be attracted to) the available carbon sites in the order from highest to lowest electron density, i.e., the order from highest to lowest nucleophilicity. Qualitatively, this is indeed what is observed when the electron density of Fig. 17, p. 53 is compared to the isomer distribution of Table 6, p. 52 , i.e., the electron density order and the isomer distribution order are equivalent -- m > o > p for both. (A more definitive quantitative view of this picture will be given later.)

The alternative approach to the one above is to consider a representation of the intermediate benzenium ion. In the case of the chlorination of nitrobenzene, we approached the problem by considering the chlorobenzenium ion. When a CNDO/2 calculation is performed for this ion, the results of Fig. 18, p. 54 are obtained. In our present context the problem becomes: where should a nitro group be placed on the chlorobenzenium ring in order to destabilize the positive charge of the ion the least? The answer is revealed in Fig. 18, p. 54 to be m > o > p, relative to the chloronium ion substituent. This, of course, agrees with the previous results obtained by consideration of the substrate. According to the Hammond postulate, this is interpreted as a contradiction which we cannot completely explain.

Table 6 . Isomer Distributions of the Chlorination
of Nitrobenzene

Solvent and Catalyst	% ortho	% meta	% para	o/2p	m/2p	m/o
Ag^+, CCl_4-$HClO_4$ *	17.82	80.33	1.51	5.9	26.6	4.5
CH_3COOH **	24.28	68.54	7.14	1.7	4.8	2.8

* R. O. C. Norman and G. K. Radda, J. Chem. Soc., 3610 (1961)

** E. Baciocchi, et al., J. Amer. Chem. Soc., 94, 7030 (1972)
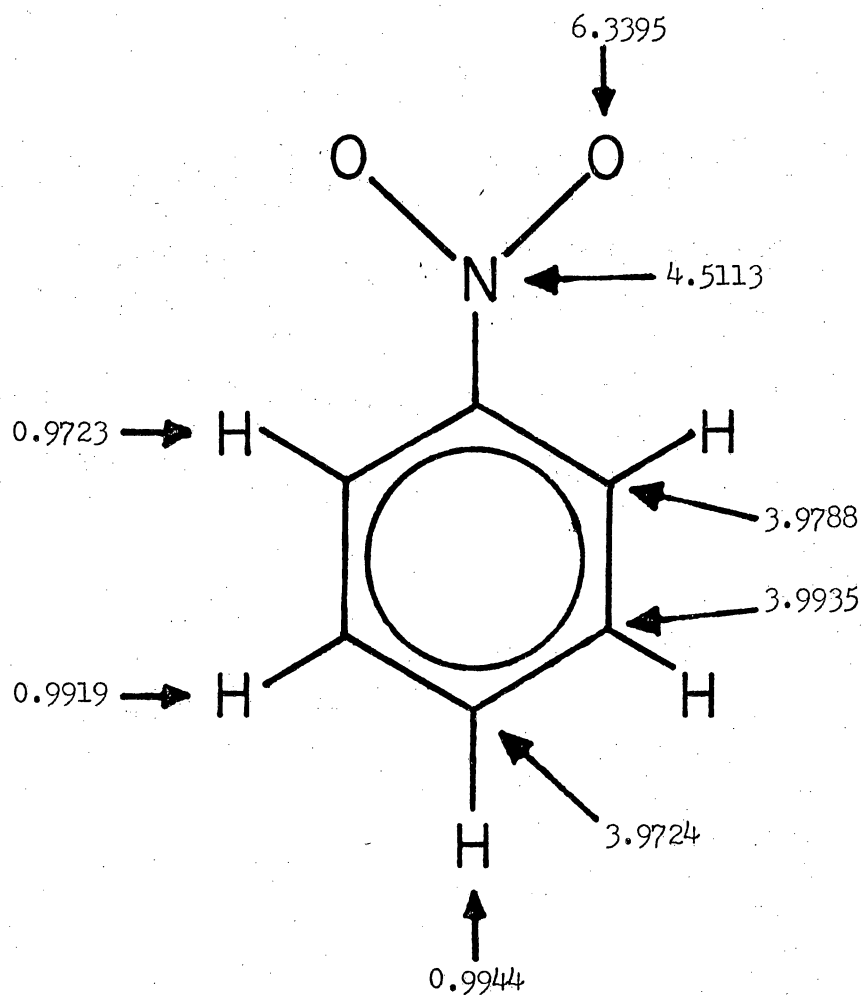
Fig. 17. All-valence-electron distribution of Nitrobenzene.
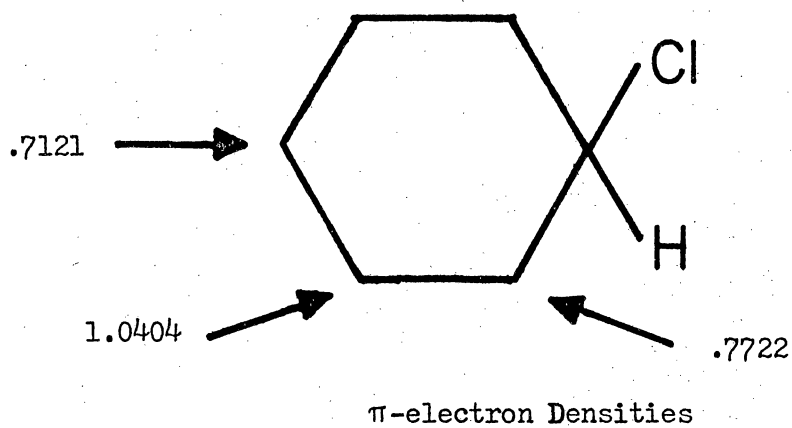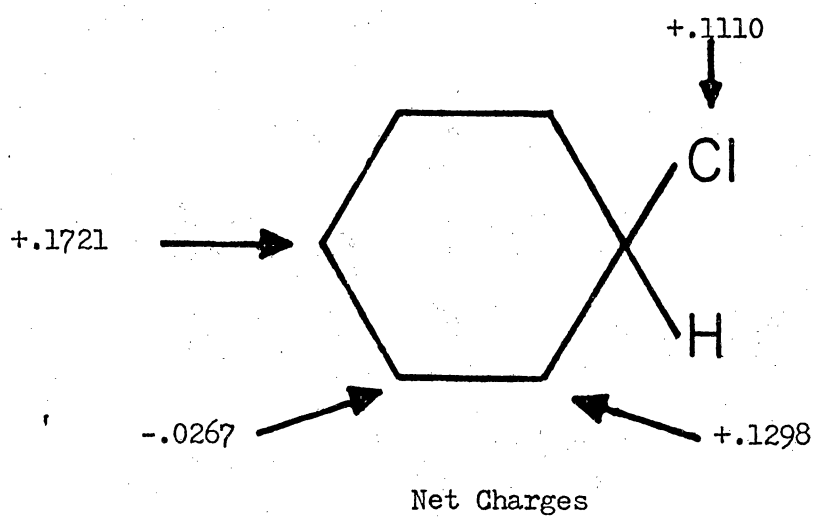
Fig. 18. Net charges and π-electron densities calculated
for the chlorobenzenium ion.

In the furtherance of our investigation of positional selectivity in the chlorination of nitrobenzene, we considered the CNDO/2 binding energies of the three isomeric forms of the chloronitrobenzenium ion intermediates. Presumably, the order of the binding energies. (a measure of stability) of the isomers of the intermediate should agree with the order of the isomer distribution of the product. (This assumes that the product distribution is controlled by the transition state of the rate-determining step and that the isomeric intermediate ions are similar to the transition states.) Three configurations for the intermediate were studied, trying to find the most realistic representation.

The first configuration consisted of a planar nitrobenzene with a chloronium ion placed above each of the available carbon positions (o-, m-, and p-chloronitrobenzenium ions) at a distance of 1.78 Å and at an angle of $90°$ to the plane of the nitrobenzene. The resulting binding energies are given in Table 7, p. 56. While the meta isomer binding energy is in the correct relative position, the ortho and para isomer binding energies are in the reversed order from that expected based upon the isomer distribution of the final product (Table 6, p.52).

The next configuration which we considered maintained the bond length and angle for the chloronium ion positions as before. The NO_2 group, however, was twisted (around the N-C bond) to several angles off the plane of the benzene ring. The results are shown in Table 8, p. 57. The hope was that the binding energy would reach a maximum for each isomer (not necessarily the same angle for each

Table 7.   Binding Energies of Attack by Cl^+ (1.78 Å above the indicated carbon atom, at an angle of 90° to the plane of the nitrobenzene; no d-orbitals on Cl^+) on Planar Nitrobenzene (Chloronitrobenzenium ion intermediates).

Position relative to NO_2	Binding Energy, kcal/mol
ortho	-4508.57
meta	-4511.90
para	-4510.26

Table 8.   Binding Energies of Attack by Cl^+ (1.78 Å above
the indicated carbon atom, at an angle of $90°$ to the plane
of the nitrobenzene; no d-orbitals on Cl^+) on Nitrobenzene
with Twisted NO_2 (Chloronitrobenzenium ion intermediates).

Angle of twist*	Binding Energies, kcal/mol.		
	ortho	meta	para
0°	-4508.57	-4511.90	-4510.26
15	--	--	-4510.64
30	-4510.01	-4512.15	-4511.52
45	--	--	-4512.46
60	-4511.21	-4511.77	-4513.28
75	--	--	-4513.85
90	-4511.21	-4511.21	-4514.10
120	-4510.14	-4511.40	--
150	-4508.88	-4511.84	--

*   As angle of twist (around the
N-C bond) increases from 0°,
O_A twists up toward the attacking
Cl^+ ion.
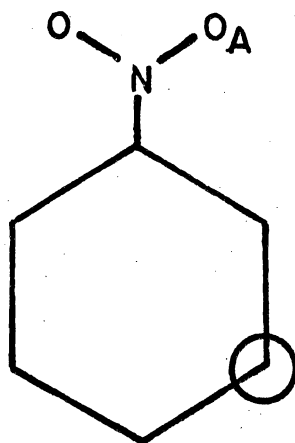
POSITION
ATTACKED

isomer). Also, the hope was that the maximum binding energies for the three isomeric ions would be in the same order as the order in the isomer distribution of the product. While the binding energies did reach maxima, the order of these binding energies is not correct. Indeed, the meta isomer binding energy is no longer in the correct relative position.

The last configuration for the chloronitrobenzenium ion intermediates involved a planar nitrobenzene with a C-Cl bond of 1.78 Å, but the Cl-C-H angle was changed to 109.5° (tetrahedral). The resulting binding energies are shown in Table 9, p. 59. While the order is maintained between this configuration and that with a planar nitrobenzene and a 90° angle, the binding energy for each isomer is less negative for this configuration than for its counterpart.

Finally, we determined the binding energies of the three isomers of the product of the overall reaction. These results are shown in Table 10, p. 60 . The hope was that this order would be the same as that in the isomer distribution of the product. Not having realized this hope, we sought some experimental measure of the relative stabilities of the isomers (e.g., heats of formation or heats of combustion) by which we could determine whether the binding energies are sufficiently accurate. Also, this would tell us whether the relative stabilities correlate directly with the isomer distribution of the product. Unfortunately, such data is apparently not available.

Table 9. Binding Energies of Attack by Cl^+ (1.78 Å from indicated carbon atom, C-Cl-H angle of 109.5°; no d-orbitals on Cl^+) on Planar Nitrobenzene (Chloronitrobenzenium ion intermediates).

Position relative to NO_2	Binding Energies, kcal/mol
ortho	-4505.55
meta	-4507.88
para	-4506.12

Table 10. Binding Energies of the Isomers of Chloronitrobenzene

Isomer	Binding Energies, kcal/mol
ortho	-4599.43
meta	-4649.44
para	-4650.13

a. Conclusion

It has become quite evident to us that studying positional selectivities (of systems more complex than propylene, for example) by the CNDO/2 method is far more complex a task than was recognized when we began. The chlorination of nitrobenzene presented some problems which we did not foresee. Some conclusions, however, were arrived at, and several recommendations for further investigation are given here.

According to the Hammond postulate, the transition state (of the rate-determining step in electrophilic aromatic substitutions, for example) should not closely resemble both the substrate and the intermediate, especially for highly exothermic or endothermic reactions. Consequently, the electron distribution of the nitrobenzene substrate and the charge distribution of the chlorobenzenium ion intermediate should not have given the same selectivity predictions. Olah (31) utilized this technique in studying electrophilic aromatic substitutions of toluene with strong and weak electrophiles and obtained valid results. Our problem with this technique may lie in the possibility that the chlorination of nitrobenzene is only slightly endothermic or exothermic. This may result in the transition state resembling both the substrate and the intermediate. Therefore, the same selectivity prediction from both would be expected. Because thermodynamic data for this reaction are not available, we cannot confirm our tentative conclusion. Consequently, the necessary enthalpy measurements should be made.

Another possibility in this regard which some may consider is that the calculated electron distributions are not sufficiently accurate. This is probably not the situation here because the parameters used (which Pople compiled) are based upon experimental observations (C^{13} n.m.r.). Also, the calculated dipole moment of 5.3D compares favorably with the experimental value of 4.3D (32)

One obvious possible reason for the failure of the binding energies of the intermediates and the final product to conform to the isomer distribution of the product may be the poor choice of geometric data (bond lengths and bond angles). A definitive determination of the geometries of nitrobenzene in the liquid phase and the chloronitrobenzene isomers in the solid phase should be done. While we know that solid nitrobenzene is planar, the liquid phase may have a twisted NO_2 group. Also, while we know that m-chloronitrobenzene is planar (33), we do not know the bond lengths and other angles; and we know nothing definitive about the ortho and para isomers.

Because definitive geometric data for the intermediates are difficult if not impossible to determine, a much more detailed study of these geometries is needed. Programs exist which optimize geometries to obtain the most stable configuration (34).

Another possibility for the failure of the binding energies may be that the CNDO/2 approximation is not sufficiently accurate. The heats of formation or the heats of combustion should be determined experimentally for the isomers of chloronitrobenzene so that they can be compared to the binding energies for accuracy.

Another way of testing the accuracy of the CNDO/2 approximation in the chlorination of nitrobenzene would be to compare the calculated binding energies of the chloronitrobenzenium ions with the experimentally determined heats of formation of the ions. These heats can be determined by techniques of mass spectrometry. The appearance potentials at which the ions are formed by the reaction in Fig. 19, p. 64 are added to the heats of atomization to give the heats of formation of the three isomers of the intermediate.

Just a word is in order about why we obtained less negative binding energies for the intermediates when we changed the Cl-C-H angle from 90° to 109.5° but maintained the planarity of the nitrobenzene. We concluded that neither configuration represents the true intermediate or local minimum on the potential energy surface for this reaction. Instead, one of the configurations (we cannot be sure which) occurs before the minimum while the other occurs after it. Another alternative is that neither of these configurations lies on the reaction path. A geometry optimization program should be used to locate the true minimum and therefore the true intermediate ions.

When we began these studies of selectivity, we assumed that binding energies could be used as an indicator of relative stabilities. The results obtained when the NO_2 group of the chloronitrobenzenium ions was twisted raise some questions about this assumption. The m- and p-isomers have their highest absolute binding energies with a twist of 90°. While we cannot be certain because definitive geometric data are not available, it is reasonable to suppose that these isomers do not exist with such a twist (e.g., m-chloronitrobenzene is untwisted).
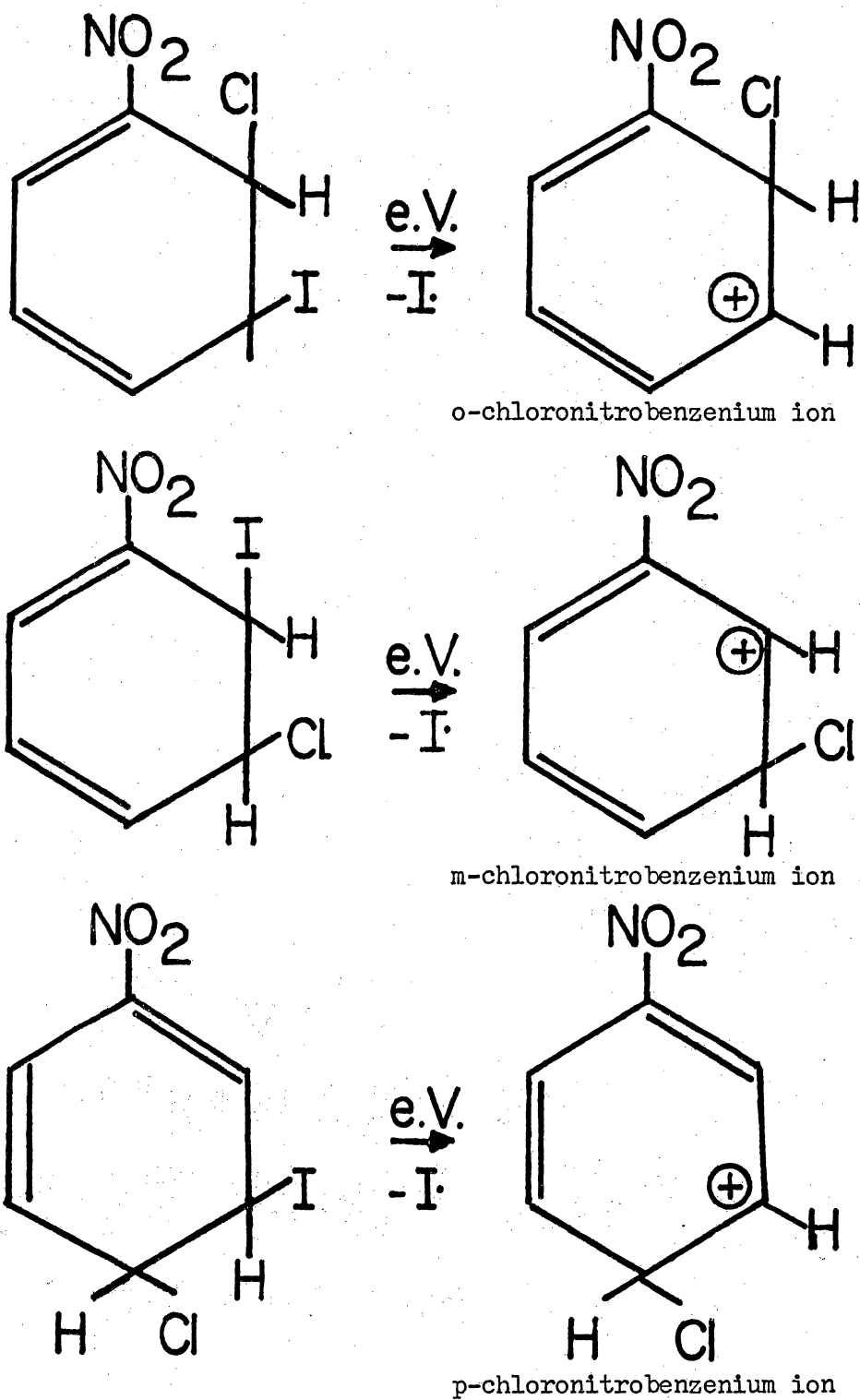
Fig. 19. Mass Spectrometric Formation of the Chloronitro-
benzenium Ion Intermediates.

Also, all of the isomers show increased stability with increase in the twist (see Table 8, p. 57). One possibility is that we are observing different geometries at different temperatures (or some other experimental factor) and that the apparent increase in stability with increased twist is really different stabilities at different temperatures, etc. That is, at room temperature the m-isomer is untwisted; but at 100°, say, it might exist with a twist of 30°. Therefore, according to this argument it is not valid to consider increased binding energies unless it can be justified by an experimental factor. This appears to be what these results are telling us. In support of this proposition is the observation of increased absolute binding energy for nitrobenzene when the NO_2 group is twisted from 0° to 90° (see Table 11, p. 66). While we know that it exists in a planar configuration at room temperature (solid phase), it may exist with increasing twist in the NO_2 group at increasingly higher temperatures.

One last possible reason for the failure of binding energies of the intermediates to agree with the isomer distribution of the product may lie with the ortho effect (35) which is the enhancement of ortho substitution. After presenting some conclusions of Olah (36) which deal with electrophilic aromatic substitutions in general, experimental data will be given which will tend to support the proposition of the ortho effect. Also, a theoretical basis for its presence will be given. Finally, it will be shown why the presence of the ortho effect would give no satisfactory correlation between the binding energies and the isomer distribution.

Table 11 . Binding Energies of Nitrobenzene with a Twisted NO_2 Group

Angle of Twist	Binding Energies, kcal/mol
0°	-4715.98
15	-4716.17
30	-4716.55
45	-4716.86
60	-4717.05
75	-4717.11
90	-4717.11

Based upon certain experimental data, Olah presents the mechanism of Fig. 20, p. 68 as an alternative to that shown in Fig. 16, p. 50 . He concludes that highly exothermic electrophilic aromatic substitutions yield a predominance of ortho over para substitution (metal ignored for the present). Such a situation occurs with strong electrophiles and substrates with nucleophilicities equal to or exceeding that of toluene. Conversely, with decreasing electrophilicity or nucleophilicity the amount of para substitution becomes more dominant until the o/p ratio (statistically corrected) becomes less than one. These reactions are increasingly endothermic.

From Table 6, p. 52 it can be seen that ortho substitution does predominate over para even under quite different experimental conditions. Based upon Olah's conclusions one would expect the chlorination of nitrobenzene with an Ag^+, CCl_4-$HClO_4$ catalyst to be certainly exothermic and with an acetic acid catalyst to be probably exothermic, although less so. With certain thermodynamic data (enthalpies) this could be confirmed.

The problem can be reduced to showing that Olah's conclusions alone do not account for the experimental data of Table 6, p. 52 and the ortho effect is a reasonable adjunct for such explanation. Table 12, p. 69 shows that the chlorination of toluene with decreasingly electrophilic chlorine does indeed proceed from predominant ortho substitution to predominant para substitution as Olah predicts. If we compare the chlorination of toluene with $FeCl_3$ as catalyst with the chlorination of nitrobenzene with the Ag^+, CCl_4-$HClO_4$ catalyst (both catalysts give the same electrophilic chlorine), we see that

nitrobenzene

"outer" complex

π-complex

m-chloronitrobenzenium ion

m-chloronitrobenzene
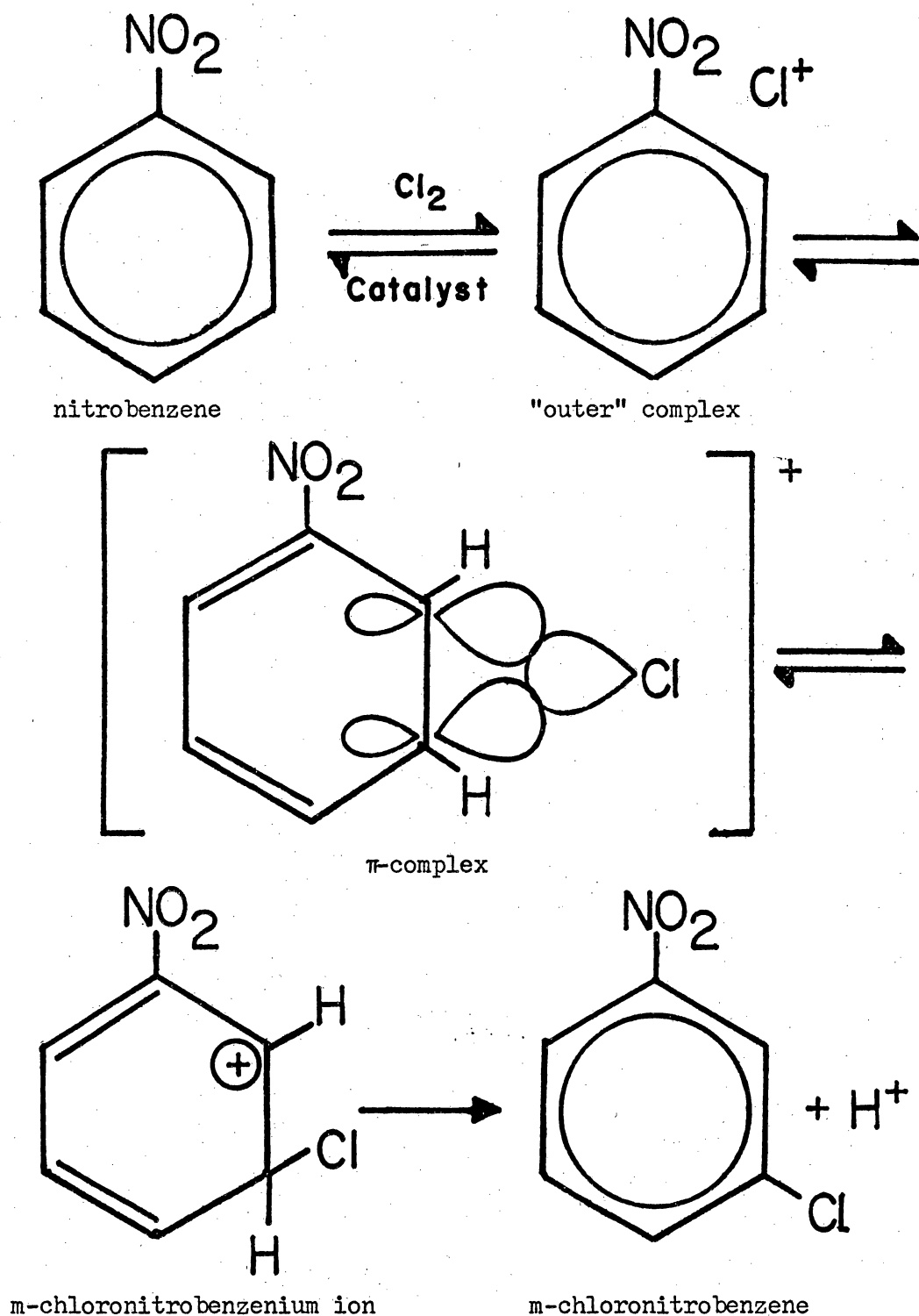
Fig. 20. Mechanism of the Chlorination of Nitrobenzene (Only production of the meta isomer is shown.). (G. Olah, Accts. Chem. Res., 4, 240 (1971).)

Table 12. Isomer Distributions of the Chlorination of Toluene.[*]

Solvent and Catalyst	% ortho	% meta	% para	o/2p	m/2p	m/o
CH_3NO_2, $FeCl_3$	67.8	2.3	29.9	1.1	.03	.03
CH_3COOH, H^+	59.8	0.5	39.7	.75	.006	.008
CH_3CN, H^+	37.6	0.5	62.4	.30	.004	.013
CH_3NO_2, H^+	33.6	.15	66.4	.25	.011	.044

[*] G. Olah, Accts. Chem. Res., 4, 240 (1971).

ortho substitution still predominates with nitrobenzene even though it is a much weaker nucleophile than toluene. This contradicts what Olah would predict. (It should be noted that the o/p ratio for nitrobenzene is about six times that for toluene which is even more striking than the purely qualitative fact.)

When acetic acid is used in the chlorination of toluene the o/p ratio is reduced to less than one (when statistically adjusted); however, under the same conditions this ratio remains greater than one for nitrobenzene (admittedly reduced). This is absolutely incredible when one realizes that NO_2 is supposed to be the best "deactivating" group (electron withdrawer). The combination of a weak electrophile (acetic acid catalyzed chloronium ion) and a weak nucleophile (nitrobenzene) again contradicts Olah.

Also, of course, when the weak nucleophile, nitrobenzene, is chlorinated with the acetic acid catalyst o/p is still greater than one even though such an electrophile is weaker than that formed with the Ag^+, CCl_4-$HClO_4$ catalyst.

The above observations certainly show that Olah's conclusions are not sufficient to account for the amount of ortho substitution in the chlorination of nitrobenzene. An explanation is the ortho effect. More specifically, the electron distribution of nitrobenzene (see Fig. 17, p. 53) shows that the oxygens of the NO_2 group are negatively charged. Electrostatic or covalent bonding can occur between one of the oxygens (n-donor) and the positively charged (or empty p-orbital of) electrophile (chloronium ion). When this occurs, the electrophile is held near the ortho carbon, thus permitting a better opportunity

for reaction. (This increased opportunity for reaction can be viewed
as either a time factor in which the electrophile has more time to
react with the ortho position of the substrate, or it can be viewed
as energetically more favorable.) Substitution at the para position
does not have this enhancement because of distance from the NO_2 group.
Also, substitution at the meta position is obviously high because of
the relatively high electron density at this position.

Olah tested this idea by performing NO_2^+ salt nitrations of
nitrobenzene with different strengths of acids present. From Table
13 , p. 72 it can be seen that the amount of ortho substitution
decreases as the acid strength increases until para substitution
becomes dominant. He believes that protonation of the NO_2 group
oxygens reduces its ability to attract the electrophile (act as an
n-donor). By the way, these results greatly reduce the validity of
considering the electron distribution of the substrate in trying
to predict selectivity. Obviously, these results do not necessarily
say anything about the chlorination of nitrobenzene. Therefore, such
work should be done to see whether similar results are obtained.

Another way of demonstrating the existence of the ortho effect
is by considering the electron density of nitrobenzene and comparing
it with the o/p, m/p, and m/o ratios. (The data to follow from
Table 6, p. 52 and Fig. 17, p. 53 .) It is reasonable to assume that
the electrophile will be attracted to the possible carbon positions
in the order from highest to lowest electron density of the substrate
and that this would be reflected in the isomer distribution of the
final product. (This ignores the Hammond postulate as a standard for

Table 13.   Nitronium Salt $(NO_2\ PF_6^-)$ Nitrations of Toluene
with Aprotic or Protic Acids.*

Aprotic and Protic Acids	% ortho	% meta	% para
CH_3NO_2	10.0	88.5	1.5
96% H_2SO_4	7.1	91.5	7.4
FSO_3H-SbF_5	4.4	90.0	5.6

* G. Olah, Accts. Chem. Res., 4, 240 (1971).

whether to consider the substrate or intermediate.) First, consider

the meta and para positions. This is a reasonable starting point

because there is no reasonable possibility of an ortho effect

influencing this ratio over the electron densities of the two

positions. The difference in the electron densities is .0211 (absolute

value) while the m/p ratio (for Ag^+, CCl_4-$HClO_4$ catalysis) is 26.6

which is a reasonable result. The difference in the electron

densities of the ortho and para positions is .0064 while o/p = 5.9.

The difference between the meta and ortho positions is .0147 while

m/o = 4.5. It can be seen that m/o almost equals o/p; however, the

two differences in the electron densities of the respective positions

are quite large. It is my conclusion that o/p is larger than it

should be because of enhanced ortho substitution while m/o is

smaller than it should be for the same reason. This enhanced ortho

substitution is the result of the picture presented earlier, and

therefore no such enhancement is expected at the meta and para

position.

Finally, a molecular orbital picture can be used to justify the

existence of the ortho effect if one alleges its existence. Zimmerman

(37) has developed an alternative to the Woodward-Hoffman rules (38)

to show symmetry allowed or disallowed systems.

Very briefly, one starts with a basis set of atomic orbitals

which represents the system under consideration. This orbitals are

arranged in a cyclic system. (One must be able to visualize such a

cyclic system for the transition state of his compound.) If there are

zero or an even number of nodes and a 4n+2 (Hückel) number of electrons,

the system is allowed. Also, if there are an odd number of nodes and a 4n (Möbius) number of electrons, the system is allowed. Otherwise, a system is disallowed.

We can apply this idea to the transition state of the chloroination of nitrobenzene at the ortho position. Figure 21, p.75 shows one node and eight electrons (a 4n number) which is allowed. Figure 22, p. 76 also shows an allowed system with four electrons and one node.

Consequently, an interaction between the oxygen of the NO_2 group and the chloronium ion electrophile (ortho effect) can be represented by an electrostatic picture and a molecular orbital picture. Both of these pictures occur in the transition state of the rate-determining step. This is a possible reason for the failure of the binding energy calculations to agree with the isomer distributions. The representations of the intermediates and the product do not involve this picture. Therefore, the binding energies which represent stability are not affected by this. Even though we were able to show the probable existence of the ortho effect, we were unable to construct a model using binding energies. While the above reason may be the case of this, much additional work should be done.
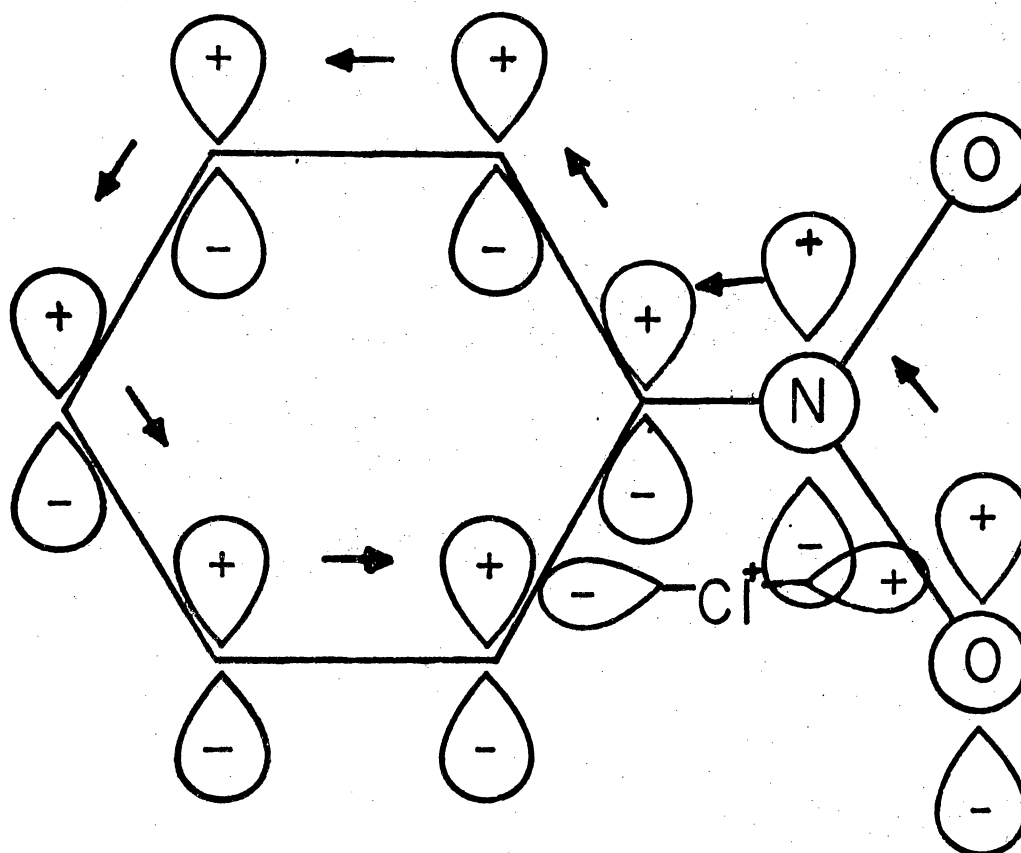
Fig. 21. Symmetry Allowed, Möbius System for the Ortho Effect in the Chlorination of Nitrobenzene (8 π-electrons and 1 node).
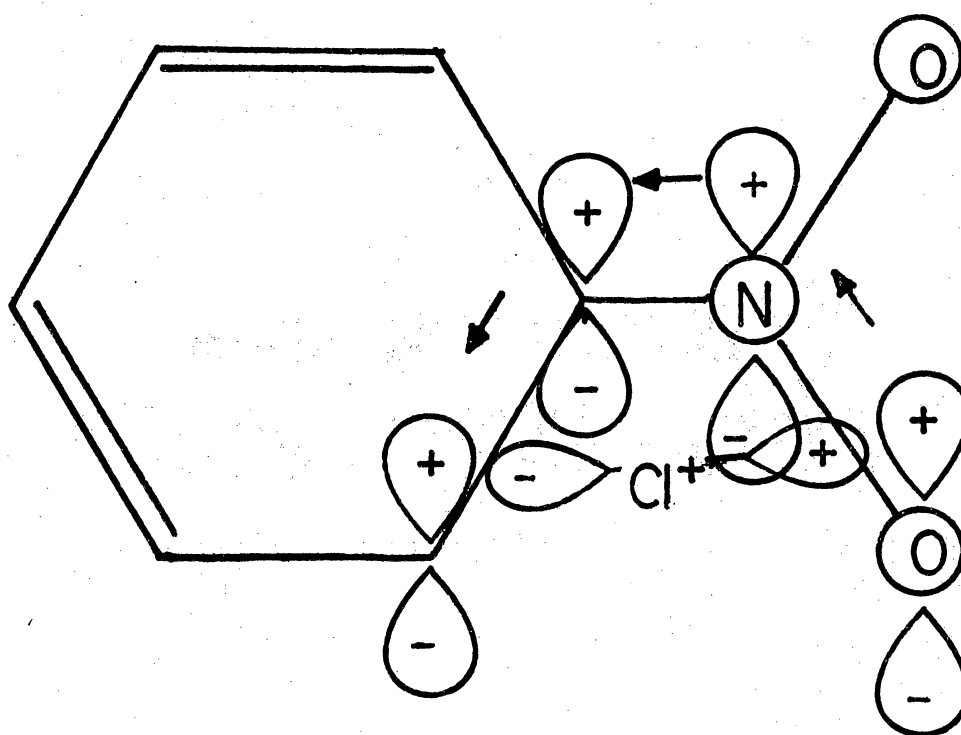
Fig. 22. Symmetry Allowed, Möbius System for the Ortho Effect
in the Chlorination of Nitrobenzene (4 π-electrons and 1 node).

3. The Chlorination of m-Chloronitrobenzene

The chlorination of m-chloronitrobenzene is an extremely interesting example of the apparent effect of the ortho effect in completely canceling the effect of the electron distribution of the substrate in controlling the isomer distribution of the product. We, here too, sought to investigate selectivity in this reaction by means of binding energies.

The reaction is shown in Fig. 23, p. 78 (39). (The mechanism is the same as previously given in Figs. 16, p. 50, and 20, p. 68.) From the electron distribution of chloronitrobenzene in Fig. 24, p. one would expect substitution in the order $C_6 > C_4 > C_3 > C_2$.

The binding energies for the various dichloronitrobenzenium ion intermediates are given in Table 14 , p. 80. A planar m-chloronitrobenzene was used with a chloronium ion 1.78 Å away from the respective carbon and at an angle of $90°$ to the plane of the substrate. The results of some twisting of the NO_2 group are also shown.

Because of the failure of the nitrobenzene calculations possibly resulting from unsatisfactory geometry data, a complete set of calculations were not done. The same unsatisfactory geometry was the cause.

The only conclusion which can be drawn is that the ortho effect is in effect here as shown in the experimental data.
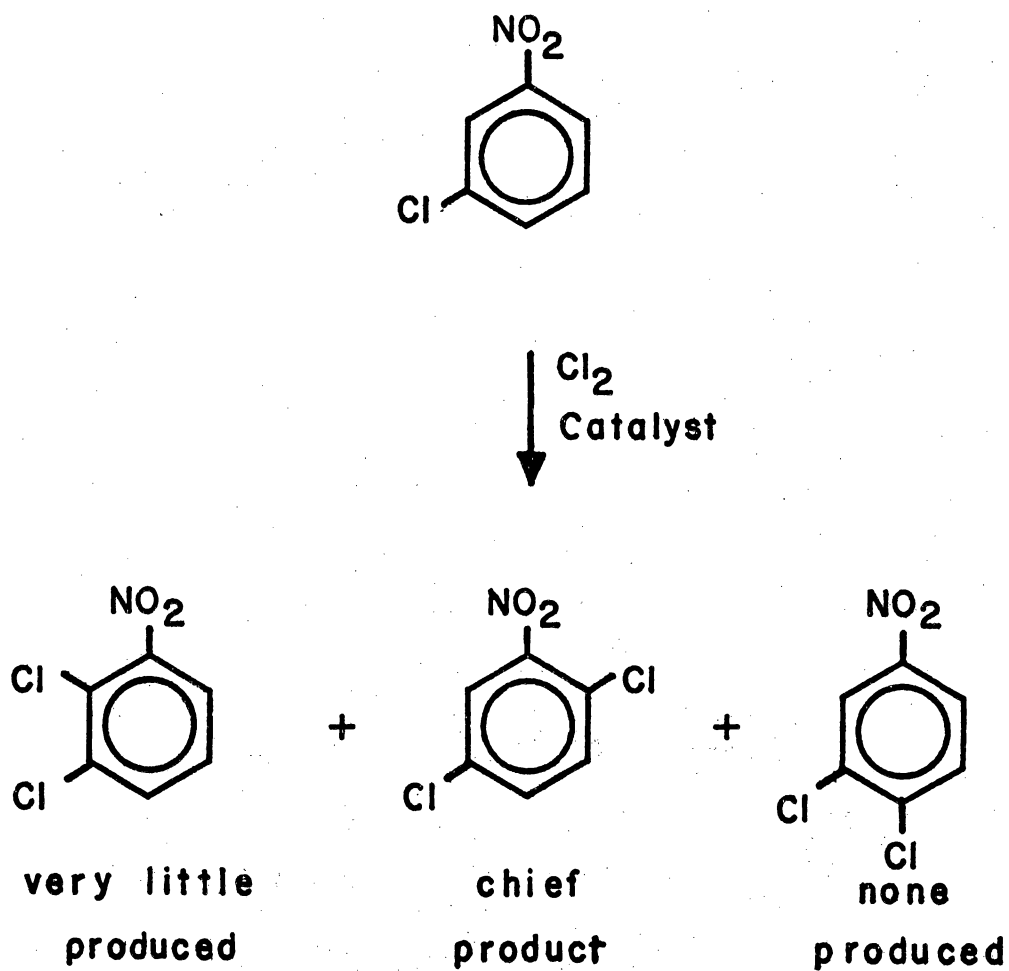
Fig. 23. Chlorination of m-Chloronitrobenzene
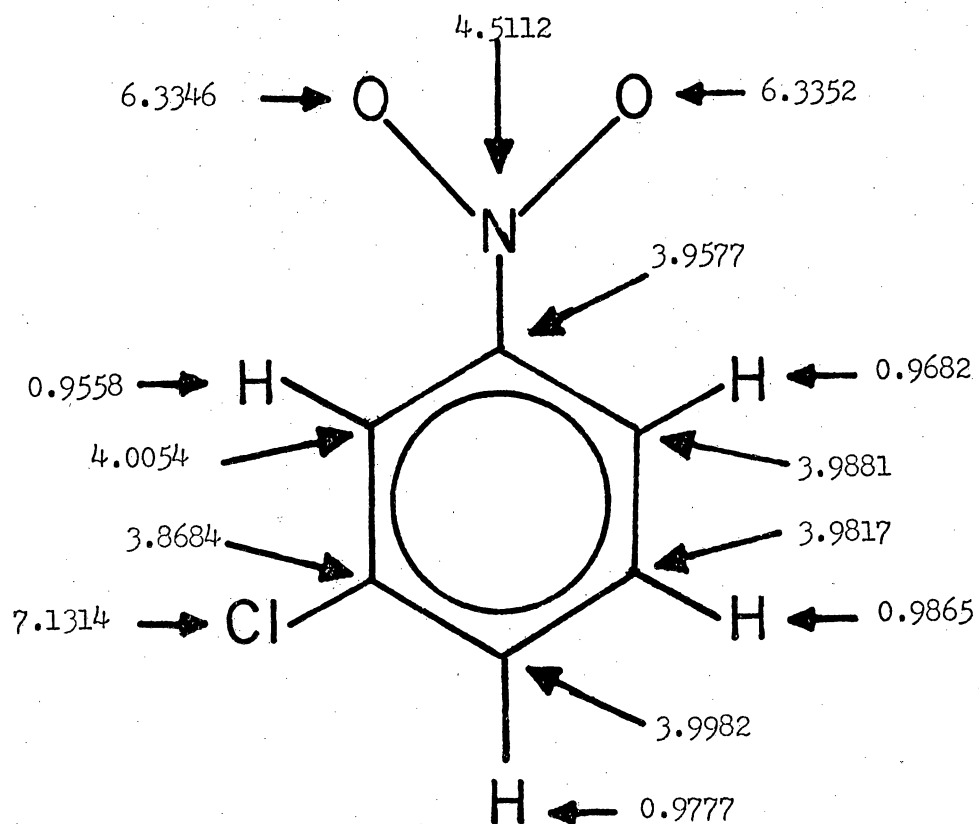
Fig. 24. All-valence-electron Distribution of
m-chloronitrobenzene.

Table 14 . Binding Energies of Attack by Cl^+ (1.78 Å from indicated carbon atom at an angle of $90°$ to the plane of the ring; no d-orbitals on the chlorines) on m-chloronitrobenzene with Twisted NO_2 (Dichloronitrobenzenium ion intermediates).

Angle of Twist[*]	Binding Energies, kcal/mol Position[**]		
	c_2	c_4	c_6
$0°$	-4437.32	-4437.51	-4435.93
20	-4438.13	--	-4436.75
40	-4439.20	--	-4437.76
60	-4439.89	--	-4438.38

* Effect of rotating NO_2 group out of plane towards
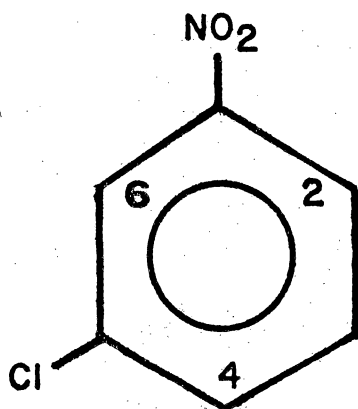
V. Conclusion

McWeeny's use of the steepest descent method in solving the Hartree-Fock equations is not as yet the "zeitgeist" for obtaining convergence in SCFMO calculations. It is, however, a major advance in working with such calculations.

The method enables one to obtain convergence with systems which heretofore always diverged. The charge-transfer complex caculations at short distances and the calicene dianion are excellent examples of this situation. Also, while the orthodox method gives the molecular orbitals which are not physically relevant, McWeeny's method directly gives the bond order and charge density matrix with which other physical properties can be determined and which gives the only unique electronic picture of the system.

The method also has flaws. In theory, one would expect the calculations to converge in the fewest possible number of iterations because the foundation of the method is to seek the energy minimum by the shortest path along the energy surface of the system. However, this occurs only for a few iterations. When the path gets to within a certain region near the minimum, the path greatly slows its approach to the minimum and therefore convergence. In our calculations with p-benzoquinone, the path veered from the minimum. Another flaw in the method is that it could conceivably proceed to an excited state minimum instead of the ground state minimum.

More work in applying the method to other systems in order to obtain more properties of its behavior should be done. A more detailed

investigation into its flaws should be done to find the reasons for them and to find solutions for them. The technique of averaging the S-matrices (see II and III) worked for the p-benzoquinone calculations in obtaining more rapid convergence, however, hindered convergence for all other considered systems. McWeeny said that it helped in obtaining convergence for his systems. The reasons for these observations should be investigated.

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Appendix

Subroutine for McWeeny's Method, Followed by Diagonalizations

```
      SUBROUTINE SCFMCW
C     MCWEENY MODIFICATION FOLLOWED BY DIAGONALIZATIONS
C      MCWEENY METHOD
C     CNDO/INDO CLOSED SHELL SCF SEGMENT                               00001880
C     GAMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q AND 00001890
C     UPPER TRIANGLE OF A, AND INITIAL DENSITY MATRIX CONTAINED IN B   00001900
C     OPTIONS CNDO OR INDO                                             00001910
      IMPLICIT REAL*8(A-H,O-Z)                                         00001920
      COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)                         00001930
      COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N                00001940
      COMMON/GAB/XXX(400),G(35,35),Q(80),YYY(80),ENERGY,XXY(214)       00001950
      COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB     00001960
      COMMON/OPTIOM/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN         00001970
      COMMON/CORE/G1(18),F2(18),ENEG(18,3),BETA0(18)                   00001980
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN               00001990
      INTEGER CHARGE,OCCA,OCCB,UL,ULIM,U,AN,CZ,Z                       00002000
      DIMENSION S(80,80),SQU(80)
      EQUIVALENCE (S(1,1),D(1,1))
      Z=0                                                              00002010
       TEST=1.0D-05
      TEST=1.0D-04
      IDIG=0
      IT=30
      RHO=1.D-8                                                        00002030
   10 CONTINUE                                                         00002040
      Z=Z+1                                                            00002050
      ENERGY=0.DO                                                      00002060
C     TRANSFER CORE HAMILTINIAN TO LOVER TRIANGLE OF A                00002070
      DO 20 I=1,N                                                      00002080
      A(I,I)=Q(I)                                                      00002090
      DO 20 J=I,N                                                      00002100
   20 A(J,I)=A(I,J)                                                    00002110
```

```
      DO 30 I=1,N                                                      00002120
      II=U(I)                                                          00002130
      A(I,I)=A(I,I)-B(I,I)*G(II,II)*0.5D0                              00002140
      DO 30 K= 1,N                                                     00002150
      JJ=U(K)                                                          00002160
30    A(I,I) = A(I,I) + B(K,K)*G(II,JJ)                               00002170
      NM=N-1
      DO 40 I=1,NM
      II=U(I)
      LL=I+1                                                           00002210
      DO 40 J=LL,N                                                     00002220
      JJ=U(J)                                                          00002230
40    A(J,I)=A(J,I)-B(J,I)*G(II,JJ)*0.5D0                             00002240
C        INDO MODIFICATION                                             00002250
      IF(OPTION.EQ.CNDO) GO TO 90                                      00002260
   50 DO 80 II=1,NATOMS                                                00002270
      K=AN(II)                                                         00002280
      I=LLIM(II)                                                       00002290
      IF(K.EQ.1) GO TO 80                                              00002300
 60     PAA=B(I,I)+B(I+1,I+1)+B(I+2,I+2)+B(I+3,I+3)                   00002310
      A(I,I)=A(I,I)-(PAA-B(I,I))*G1(K)/6.D0                           00002320
      DO 70 J=1,3                                                      00002330
      A(I+J,I+J)=A(I+J,I+J)-B(I,I)*G1(K)/6.D0-(PAA-B(I,I))*7.D0*      00002340
     1F2(K)/50.D0+B(I+J,I+J)*11.D0*F2(K)/50.D0                        00002350
 70     A(I+J,I)=A(I+J,I)+B(I,I+J)*G1(K)/2.D0                         00002360
      I1=I+1                                                           00002370
      I2=I+2                                                           00002380
      I3=I+3                                                           00002390
      A(I2,I1)=A(I2,I1)+B(I2,I1)*11.D0*F2(K)/50.D0                    00002400
      A(I3,I1)=A(I3,I1)+B(I3,I1)*11.D0*F2(K)/50.D0                    00002410
      A(I3,I2)=A(I3,I2)+B(I3,I2)*11.D0*F2(K)/50.D0                    00002420
   80 CONTINUE                                                         00002430
```

```
      90 CONTINUE                                                            00002440
         DO 100 I=1,N                                                        00002450
 100     ENERGY = ENERGY + .5D0*B(I,I)*( A(I,I)+Q(I) )                       00002460
         DO 105 I=1,NM                                                       00002470
         LL=I+1                                                              00002480
         DO 105 J=LL,N                                                       00002490
 105     ENERGY = ENERGY + B(I,J)*( A(I,J)+A(J,I) )                          00002500
         WRITE(6,110) ENERGY                                                 00002510
 110     FORMAT(//,10X,21H ELECTRONIC ENERGY    ,F16.10)                     00002520
         IF(DABS(ENERGY-OLDENG).GE..000001D0) GO TO 150                      00002530
 120     Z=IT+1
 130     WRITE(6,140)                                                        00002550
 140     FORMAT(5X,18H ENERGY SATISFIED /)                                   00002560
         GO TO 170                                                           00002570
 150     CONTINUE                                                            00002580
         DELE=ENERGY-OLDENG
 160     OLDENG=ENERGY                                                       00002590
         IF(DABS(DELE).LE.TEST.OR.Z.GT.22.OR.IDIG.EQ.1) GO TO 170
         NNN=N
         DO 153 I=1,NNN
         DO 153 J=1,NNN
         S(I,J)=0.0
         DO 153 K=1,NNN
         FIK=A(I,K)
         IF(K.GT.I) FIK=A(K,I)
         S(I,J)=S(I,J)+FIK*B(K,J)*0.5
         DO 153 L=1,NNN
         FKL=A(K,L)
         IF(L.GT.K)  FKL=A(L,K)
         S(I,J)=S(I,J)-B(I,K)*FKL*B(L,J)*0.25
 153     CONTINUE
         AA=0.0
```

```
      BB=0.0
      CC=0.0
      DO 155 I=1,NNN
      DO 155 J=1,NNN
      II=U(I)
      JJ=U(J)
      GIJ=G(II,JJ)
      FIJ=A(I,J)
      IF(J.GT.I) FIJ=A(J,I)
       DO 154 K=1,NNN
  154 BB=BB+FIJ*(S(J,K)+S(K,J))*(S(K,I)-S(I,K))
      AA=AA+FIJ*(S(I,J)+S(J,I))
  155 CC=CC+GIJ*(8.0*S(I,I)*S(J,J)-(S(I,J)+S(J,I))**2)
      OPTLAM=-AA/(2.0*BB-CC)
      DO 157 I=1,NNN
      DO 157 J=1,NNN
      B(I,J)=B(I,J)-OPTLAM*(S(I,J)+S(J,I))*2.0
      DO 156 K=1,NNN
  156 B(I,J)=B(I,J)-(OPTLAM**2)*(S(I,K)+S(K,I))*(S(K,J)-S(J,K))*2.0
  157 CONTINUE
      IDMAX=3
      DO 159 IMM=1,IDMAX
      DO 158 I=1,NNN
      DO 158 J=I,NNN
      S(J,I)=0.0
      DO 1580 K=1,NNN
 1580 S(J,I)=S(J,I)+B(I,K)*B(K,J)*0.25
      IF(I.EQ.J) SQU(I)=S(J,I)
      S(I,J)=0.0
      DO 1581 K=1,NNN
      DO 1581 L=1,NNN
 1581 S(I,J)=S(I,J)+B(I,K)*B(K,L)*B(L,J)*0.125
```

```
C       B**2 IS IN LOWER HALF,   B**3 IS IN UPPER HALF
  158 CONTINUE
      DO 1582 I=1,NNN
      LL=I+1
      B(I,I)=(3.0*SQU(I)-2.0*S(I,I))*2.0
      DO 1582 J=LL,NNN
      B(I,J)=(3.0*S(J,I)-2.0*S(I,J))*2.0
 1582 B(J,I)=B(I,J)
  159 CONTINUE
      CALL SCFOUT(0,2)
      GO TO 299
  170 CONTINUE                                                          00002600
      IDIG=1
      IF (Z.LE.IT) GO TO 210                                           00002610
C     SYMMETRIZE F FOR PRINTING (MATRIX A)                             00002620
  180 DO 190 I=1,N                                                     00002630
      DO 190 J=I,N                                                     00002640
  190 A(I,J)=A(J,I)                                                    00002650
      WRITE(6,200)                                                     00002660
  200 FORMAT(1X,27H HARTREE-FOCK ENERGY MATRIX)                        00002670
      CALL SCFOUT(0,1)                                                 00002680
  210 CONTINUE                                                         00002690
      CALL EIGN(N,RHO)                                                 00002700
      IF (Z.EQ.1) CALL SCFOUT(1,2)                                     00002710
      IF (Z.LE.IT) GO TO 240                                          00002720
  220 WRITE(6,230)                                                    00002730
  230 FORMAT(1X,28HEIGENVALUES AND EIGENVECTORS   )                   00002740
      DO 235 I=1,N                                                     00002750
      DO 235 J=1,N                                                     00002760
  235 D(I,J)=B(I,J)                                                    00002770
      CALL SCFOUT(1,2)                                                 00002780
  240 CONTINUE                                                         00002790
```

```
C         EIGENVECTORS ( IN B ) ARE CONVERTED INTO DENSITY MATRIX (IN B)        00002800
          DO 280 I=1,N                                                          00002810
          DO 260 J=I,N                                                          00002820
          XXX(J)=0.0D0                                                          00002830
          DO 250 K=1,OCCA                                                       00002840
      250 XXX(J)=XXX(J)+B(I,K)*B(J,K)*2.0D0                                     00002850
      260 CONTINUE                                                              00002860
          DO 270 J=I,N                                                          00002870
      270 B(I,J)=XXX(J)                                                         00002880
      280 CONTINUE                                                              00002890
          DO 290 I=1,N                                                          00002900
          DO 290 J=I,N                                                          00002910
      290 B(J,I)=B(I,J)                                                         00002920
      299 IF(Z.LE.IT) GO TO 10
      300 CONTINUE                                                              00002940
          RETURN                                                               00002950
          END                                                                  00002960
```

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A STUDY OF THE USE OF A STEEPEST DESCENT TECHNIQUE IN THE
SOLUTION OF THE HARTREE-FOCK EQUATIONS AND ITS APPLICATION
TO SELECTED SYSTEMS

by

Keith Allen Levinson

(ABSTRACT)

McWeeny has developed a method which utilizes the steepest descent
technique in sloving the Hartree-Fock equations. The mathematical
development is presented and discussed. The method achieves
convergence for several otherwise recalcitrant systems.

The following systems are investigated and discussed:

1. the π-electron systems of p-benzoquinone and calicene,

2. the all-valence-electron systems of the calicene dianion,
    nitrobenzene and m-chloronitrobenzene,

3. the first complete SCFMO binding energy curves for the Cl_2-
    benzene charge-transfer complex, including several config-
    urations,

4. studies of selectivity for the protonation of (addition of
    Bronsted acids to) propylene, and the chlorination of
    nitrobenzene and m-chloronitrobenzene (These studies proved
    to be far more complex than initially foreseen, and firm
    conclusions were not obtained.).

Recommendations for further investigation of these systems are also
given.