Lawrence Berkeley National Laboratory

Recent Work

Title

THE ELECTRON SPIN RESONANCE SPECTRA OF RADICAL ANIONS IN LIQUID AMMONIA

Permalink https://escholarship.org/uc/item/2m21n4vz

Author Levy, Donald Harris.

Publication Date 1965

University of California Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

THE ELECTRON SPIN RESONANCE SPECTR OF RADICAL ANIONS IN LIQUID AMMONIA

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory Berkeley, California

AEC Contract No. W-7405-eng-48

THE ELECTRON SPIN RESONANCE SPECTRA OF RADICAL ANIONS IN LIQUID AMMONIA

Donald Harris Levy

14 1

(Ph.D. Thesis)

January 1965

CONTENTS

ለኩረ	transt		
ADE	stract	# • • • • • • • • • • • • • • • • • • •	v
I.	Intr	oduction	1
II.	Thec	ory and Chemistry of Radical Anions	:4
	Α.	Previous Theoretical Work	4
	В.	Previous Chemical Work	8
III.	Ammo	nia Systems	12
	Α.	Metal-Ammonia Solutions	L2
· ·	в.	Electrolysis in Liquid Ammonia	լկ
	C.	Chemical Reactions in Liquid Ammonia	٤5
IV.	Expe	rimental Techniques	6
	Ά.	Electrolysis Cell	_6
	B.	Cooling System	-9
	C.	ESR Spectrometer	20
	D.	Typical Procedure	21
	E.	Chemicals	23 -
v.	Resu	lts and Discussion	26
	Α.	Butadiene	26
·	Β.	Methyl and Methylene Coupling Constants	5
	C.	Justification of the Hyperconjugation Model:	' O
			Ŭ
•	D.	Nitrosobenzene and Nitrobenzene 8	3
	E.	Cyclooctatraene	9
Ackı	nowled	lgements	ı
Appe	endice	∋s	

-iii-

-iv-,

THE ELECTRON SPIN RESONANCE SPECTRA OF RADICAL ANIONS IN LIQUID AMMONIA

Donald Harris Levy

Inorganic Materials Research Division, Lawrence Radiation Laboratory, Department of Chemistry, University of California, Berkeley, California

ABSTRACT

January 1965

A new technique for the generation of pi-bonded radical anions by means of continuous electrolysis in liquid ammonia has been developed, and the experimental procedures are described in detail. The radical anion of 1,3-butadiene has been prepared by this method and its electron spin resonance spectrum has been observed. The measured proton hyperfine coupling constants are compared to those predicted by several theoretical calculations.

The radical anions of isoprene, 1,3-cyclohexadiene and 2,3-dimethylbutadiene have been prepared and their ESR spectra have been observed. A theory for deriving methyl and methylene proton coupling constants from a knowledge of the unpaired spin density distribution is developed and used to predict the coupling constants of these and other methyl and methylene containing radical anions. The unpaired spin distribution is calculated using a hyperconjugation model and several simple LCAO molecular orbital theories. A small correction for spin exchange polarization is taken into account. It is shown that a simple extension of Huckel theory can be used to successfully predict the methyl and methylene proton coupling constants of all the radical anions considered.

An inequivalence of the methylene protons in dimethylbutadiene radical anion has been observed. To explain this the usual molecular orbital treatments have been modified by using an expanded basis set including the 3d carbon atomic orbitals. These are shown to be of the correct symmetry to account for the observed anisotropy.

The radical anion of 1,3,5-cycloheptatriene has been prepared and the hyperfine coupling constants measured. The methylene proton coupling constant has been assigned by monodeuteration of the methylene group. The wavefunction of the unpaired electron in this molecule is shown to have a node at the methylene protons and consequently any hyperfine coupling is due to a combination of spin exchange polarization and electron correlation. The small contribution of electron correlation is estimated by an approximate self-consistent field calculation, and the remaining hyperfine coupling is taken as a measure of the spin exchange polarization. A correction term useful for accounting for spin polarization effects in other radicals is derived. The fact that this term is small provides a justification of the hyperconjugation model used previously.

The ESR spectra of the nitrosobenzene and nitrobenzene radical anions have been observed in liquid ammonia. The nitrosobenzene radical anion shows two ortho and two meta proton coupling constants which may be explained by either of two simple theoretical models. One model involves non-bonded interactions introducing off-diagonal Hamiltonian matrix elements between non-bonded atoms, and the other involves an electron polarization effect which produces small changes in the on-diagonal matrix elements. These have been described previously as the β - and α -effects.

-vi-

The nitrobenzene radical anion was prepared in liquid ammonia as a reference and to compare solvent shifts.

The radical anion of cyclooctatetraene was prepared in liquid ammonia and is shown to be much more stable in this solvent than in any previously used. Small coupling constant solvent shifts were observed which, because of the symmetry of the molecule, can only be attributed to a solvent perturbation of the sigma-pi interaction.

INTRODUCTION

т.

Molecular quantum mechanics and the general problem of molecular electronic structure is fundamental to all of chemistry, and it is not surprising that it has received considerable attention ever since the introduction of quantum mechanics itself. The recent general availability of high speed computing machinery has led to a proliferation of theoretical calculations which has brought this field to the point where quite sophisticated self-consistent field calculations appear in the organic chemistry literature, and the more advanced calculations of "theoretical" chemists involve so much computation that they are almost entirely divorced from conventional chemical concepts and any notion of chemical intuition. One unfortunate aspect of this wealth of theoretical computation is that the theoretician is beginning to outstrip the experimentalist and many calculations are yielding results for which the corresponding experimental data are not available. One frequently finds the theoretician forced to compare his latest calculation to the "best Hartree-Fock calculation" rather than to experimental results simply because the experimental results do not exist.

One promising source of the necessary data has been relatively new areas of radio frequency spectroscopy. Their utility lies in the fact that it usually is possible to separate out small terms from the molecular Hamiltonian which to a very high degree of approximation do not effect the molecular energy or wave function but which do contain parameters which depend upon the molecular wave function. Since these smaller terms are usually much more easily solved than the complete Hamiltonian one can obtain very accurate measurements of the values of the parameters which appear in them. If one can then relate the parameters to the molecular wave function one has a measure, at least in parts of the molecule, of the wave function itself. Coulson described these small terms as "measuring rods, able to be placed within the electronic charge-cloud without affecting it."¹

-2-

A specific technique that has provided a great deal of data of this nature has been the measurement of the electron spin resonance (ESR) spectra of organic radical ions and neutral radicals in solution. The motional narrowing of the absorption line due to the rapid tumbling in solution allows a very great degree of resolution and causes the anisotropic terms in the Hamiltonian to averge to zero, thus simplifying the interpretation of the spectrum. The interaction of the electronic and nuclear paramagnetism produces a great deal of hyperfine structure in the spectrum which can be readily analyzed in terms of a set of hyperfine coupling constants that are related to the electronic structure of the molecule. The problem of determining this relationship is complex but not impossible, and one is now able to get a reasonable estimation of the value of the molecular wave function from the measured hyperfine constants.

One of the severe restrictions on this technique is the experimental difficulty of preparing the necessary paramagnetic species. A survey of the literature impresses one with the fact that the theoreticians and the experimentalists are not working on the same kinds of molecules. This is illustrated by the fact that the molecules which are experimentally easily reducible to the radical anion are those with the larger conjugated pi-electron systems and are difficult to treat theoretically. Conversely the molecular species that are interesting and tractable theoretically are extremely unstable and difficult to prepare. Thus the theoreticians deal with such species as methyl, allyl, and ethylene while the experimentalists make measurements on anthracene, tetracene, etc. It was in an attempt to develop experimental techniques that would help close this gap between theoretician and experimentalist that the following work was undertaken.

II. THEORY AND CHEMISTRY OF RADICAL ANIONS

A. Previous Theoretical Work

As mentioned above it is possible to separate the complete molecular Hamiltonian into various terms which are non-interacting. It is customary for ESR work to write the complete Hamiltonian as

$$H = H_{0} + H'$$
 (1)

where H_o contains all the electrostatic interactions and H' contains the spin orbit, magnetic field, and hyperfine terms. Treating H' as a perturbation it is possible to derive an operator H_g (the "spin Hamiltonian") which lifts the spin degeneracy within the ground manifold of H_o . Although the coefficients of the operators appearing in H_g are averages of various orbital matrix elements, the operators themselves are spin operators and hence H_g operates only in the space of the electronic and nuclear spin variables. The derivation of H_g for atoms has been treated by Pryce,^{2,3} and has been lucidly reviewed by Bleaney and Stevens⁴ and again by Pake.⁵ Stone⁶ has shown that this treatment cannot be applied directly to molecules due to the fact that the theory is not invariant to a gauge transformation which changes the point in space about which the electronic angular momenta are referred. However, he has derived a similar theory for molecules which is gauge invariant.

The results of these treatments is that the Zeeman term of the spin Hamiltonian describing the interaction of the electronic magnetic moment and an applied magnetic field \overline{H} is given by

 $H_{g} = \beta \overline{H} \cdot g \cdot \overline{S}$

(2)

where β is the Bohr magnetron, \overline{S} is the electron spin operator, and g is a second-rank tensor which is derived from the theory and contains orbital angular momentum matrix elements arising from the spin-orbit interactions. In liquid systems the rapid tumbling of the paramagnetic species usually averages out any anisotropies in the g tensor and it may usually be replaced by a scalar, g.

In molecular radicals the low symmetry caused by the strong molecular electric field almost completely quenches any orbital magnetism, which results in the complete removal of most orbital degeneracy. Any degeneracies remaining due to whatever molecular symmetry exists tend. to be removed by the Jahn-Teller effect.⁷ The result of this is that the g-value for molecular radicals tends to be very close to 2.00229, the g-value of the free electron. While a theory⁸ has been developed to account for deviations from the free electron g-value, very little information about the electronic structure of the molecule can be obtained from these extremely small deviations.

The Hamiltonian for the interaction of the electronic and nuclear angular momenta is expressed as 9

$$H = \sum_{n} g_{e} g_{n}^{\beta\beta} \left\{ \frac{S_{e} \cdot I_{n}}{|r_{e} - r_{n}|^{3}} - \frac{3(S_{e} \cdot r)(I_{n} \cdot r)}{|r_{e} - r_{n}|^{5}} - \frac{8\pi}{3} S_{e} \cdot I_{n} \cdot \delta(r_{e} - r_{n}) \right\}$$
(3)

1.25

The notation is standard and is defined in Ref. 9. The first two terms in the brackets arise from the classical dipole-dipole interaction of the electronic and nuclear magnetic moments. It has been shown by Weissman¹⁰ that for molecules undergoing rapid tumbling in solution this part of the interaction vanishes. The term remaining arises from the Fermi contact interaction¹¹ and is not averaged out by any molecular motion. In organic: pi-radicals the energy splittings caused by this term are extremely small (of the order of 10 mc.). However as noted above these radicals have very small spin-orbit couplings and this produces long relaxation times and a very highly resolved spectrum. Consequently even these small splittings can be fully resolved and a great deal of information may be obtained.

-5-

It is easily seen that the effective spin Hamiltonian consisting of the Zeeman term and the Fermi contact term may be solved to define the position of the lines in the ESR spectrum in terms of a set of parameters A, the hyperfine coupling constants, where for the ith magnetic nucleus

$$A_{i} = \left(\frac{8 \Pi g \beta \mu_{i}}{3 I}\right) \delta_{i}$$

where

$$\delta_{\mathbf{i}} = \langle \Psi |_{\Sigma} \delta(\vec{\mathbf{r}}_{\mathbf{k}\mathbf{i}}) S_{\mathbf{k}\mathbf{z}} | \Psi \rangle / S_{\mathbf{z}}$$

In this expression $\delta(\vec{r}_{ki})$ is the Dirac delta function of the distance between electron k and nucleus i and δ_i might be looked upon as the unpaired spin density at the magnetic nucleus i. Thus from the experimental value of the coupling constant A_i one gets easily and accurately the unpaired spin density at the ith magnetic nucleus.

Unfortunately for most pi-bonded molecules this is not a very interesting quantity in itself (with certain exceptions to be treated later). The reason for this is that almost all theoretical treatments of pi-bonded molecules begin with an assumption that the pi-sigma separation approximation is valid. This approximation assumes that the total molecular wave function may be written as

$$\Psi = A[\Psi_{\sigma}\Psi_{\Pi}]$$

(6)

(4)

(5)

where Ψ_{σ} and Ψ_{Π} are functions of only the sigma and only the pi-electron coordinates (space and spin) respectively and A is the antisymmetrization operator with respect to pi and sigma electron interchange.¹² Since the unpaired electron in pi-radicals is a pi-electron in this approximation all the nuclei lie at a node of $\overline{\Psi}_{\Pi}$ and therefore the pi-sigma approximation implies that δ_i and A_i are both exactly zero. The fact that there is any hyperfine interaction observed at all indicates a departure from pi-sigma separability. Of course the minute energies involved indicate that the pi-sigma interaction is very small, and that its neglect is unimportant in comparisons with other approximations that must be made in any molecular theory. Nonetheless in order to compare experimental coupling constants with such a theory it is necessary to have an additional relationship between the experimental numbers and the wave function Ψ_{Π} .

-6-

This relationship in aromatic protons was discussed by McConnell^{13,14} who theoretically examined the hyperfine'interaction in a C-H fragment of an aromatic hydrocarbon. He postulated an exchange polarization mechanism whereby the unpaired pi-electron on the carbon atom polarized the sigma-electrons in the C-H bond resulting in a net unpaired spin density at the proton. His treatment involved admixing a small amount of an excited configuration ϕ with the ground state wave function. The configuration ϕ involved the antibonding valence bond function where the two sigma-electrons in the C-H bond have parallel spins. This treatment led to the approximate relationship

where ρ_i is the probability of finding the unpaired electron on the carbon atom to which the ith proton is bonded (frequently referred to as

(7)

5 19 11

 $A_i = Q \rho_i$

the unpaired spin density at the ith carbon atom), and Q is a constant defining the sigma-pi interaction. In both a simple valence bond or molecular orbital derivation Q is proportional to the quantity $(J_{ph}-J_{ps})/E$ where

$$J_{ps} = \langle p_1 s_2 | \frac{e^2}{r_{12}} | s_1 p_2 \rangle$$
 (8)

and E is the energy of the excited configuration above the ground configuration. Here p is a $2p_z$ atomic orbital centered on the carbon atom, h is an sp^2 hybrid orbital centered on the carbon atom and directed toward the proton, and s is the ls atomic orbital of the proton. A more complicated expression for Q has been derived using a theory generalized to the case of polyatomic pi-electron radical systems.¹⁵

Colpa and Bolton¹⁶ have extended the theory by considering the C-H fragment and including the effect of excess charge in addition to that of unpaired spin in attempt to explain certain anomalous trends which develop when Eq. (7) is applied. Their derivation has led to the relationship

$$A_{i} = (Q_{0} + k\epsilon_{i})\rho_{i}$$
(9)

where ϵ_i is the excess charge density on the ith carbon atom and K is a theoretical constant. Giacometti <u>et al</u>.¹⁷ have tried to explain these same anomalies by including nearest neighbor interactions with the C-H fragment.

The first treatment of hyperfine interaction due to magnetic nuclei other than protons was by McLachlan <u>et al</u>.¹⁸ who removed a few minor restrictions from McConnell's theory and generalized this theory to include all magnetic nuclei lying in the nodal plane of a pi-radical. The particular importance of such a theory is that now C^{13} and N^{14} splittings could also be related to the molecular electronic structure. Their theory yielded the result that

$$A_{i} = tr(Q^{i}\varrho)$$
 (10)

where ρ is the pi-electron spin density matrix and Q^1 is a hyperfine coupling matrix whose elements depend upon σ -II exchange integrals and excited sigma triplet states. An expanded theory which considered not only the C-H fragment but in addition treated the ls carbon electrons and all the electrons in the three bonds of the sp² hybridized carbon atom was developed by Karplus and Fraenkel.¹⁹ This theory, which is applicable to any many-electron atom such as N¹⁴, gave the prediction that

$$A_{i} = (S^{C} + \sum_{j=1}^{3} Q_{CX_{j}}^{C})\rho_{c} + \sum_{j=1}^{3} Q_{X_{j}C}^{C}\rho_{j}$$
(11)

Here C is an sp^2 hybridized carbon atom that is bonded to three atoms, $X_j(J = 1,2,3)$ and ρ and ρ_j (j = 1,2,3) are the pi-electron spin densities on atoms C and X_j respectively. S^C accounts for the contribution of the ls electrons of the carbon atom and the Q's for that of the remaining electrons. The theory can be used for any atom, A, by defining a set of parameters Q_{BC}^A which result from the interaction between the bond BC and the pi-electron spin density on atom B.

B. Previous Chemical Work

The first observed ESR spectra of radical anions were reported by Weissman and co-workers in a series of papers primarily concerning the naphthalene negative ion.²⁰⁻²² Since then quite a large number of papers have appeared reporting the ESR spectra of specific radicals. The literature on this subject prior to 1958 has been summarized quite nicely by

and the second second

Ingram² in his chapter on stable free radicals (Chapter 5). However much of the high resolution work in this field has been done since the publication of Ingram's book and unfortunately, to the best of the author's knowledge, no single comprehensive review of the literature since 1958 has been written. A series of annual reviews covering the previous year's work has been published²³⁻²⁷ and in some ways helps to fill this gap. A recent translation of the book by Al'tshuler and Kozyrev²⁸ gives a more recent review although his table of molecules studied is taken <u>verbatim</u> from Ingram.⁹ Carrington²⁹ has written an introductory review of this area which contains references to much of the most significant recent literature, but it is not intended to be a complete listing of all recent work. A complete bibliography of all ion-radicals studied (including subject or formula index) would be of considerable use but is unfortunately outside the scope of this work. Somewhat more to the point, there follows a brief review of the techniques developed for the generation of radical anions.

The first solutions of radical anions were prepared by the chemical reduction of the parent species (A), by alkali metals (M) using an inert ether solvent such as tetrahydrofuran (THF). The detailed experimental procedure for such chemical reductions has been described in the literature. ³⁰⁻³¹ The equilibrium reaction involved is

$$A + M = A^{-} + M^{-}$$
(12)

and in cases where the factor limiting the production of the anion is a small electron affinity for A, this technique is still perhaps the best available.

^{*}Probably the best example of the extreme reducing power of these solutions is the recent generation of the cyclopropane radical anion.³²

-9-

On the other hand, in many cases, the production of the anion is limited by other factors such as polymerization or additional reaction, and in these cases direct chemical reduction leaves something to be desired. The technique of electrolytic reduction was first used by Geske and Maki³³ for the production of the nitrobenzene radical anion and represented a considerable improvement for many interesting cases. Geske and Maki used an <u>intra muros</u> technique whereby the radicals were generated in an electrolytic cell placed directly in the microwave cavity of the ESR spectrometer. More recently Rieger <u>et al</u>.³⁴ have carried out the electrolysis outside the microwave cavity and transferred the electrolyzed solution to the cavity via a flow system.

The electrolytic method of generating negative ions has a number of distinct advantages over the older technique of chemical reduction:

1). The possibility of hyperfine interaction between the unpaired electron and the magnetic nucleus of the alkali metal used as a reducing agent is eliminated since very large cations can be used.

2). The complications of ion pairing are minimized by the use of a solvent of high dielectric constant.

3). The potential at which the reduction is carried out is easily and continuously variable.

4). The difficulty of purifying and manipulating small amounts of alkali metals is eliminated.

5). Continuous electrolysis offers the possibility of generating an observable steady state concentration of radicals that would otherwise be too reactive to observe.

Electrolytic reductions are usually carried out in a glass cell between a mercury pool cathode and some reference anode, frequently a

-10-

saturated calomel electrode. In addition to a small amount (ca. $10^{-2} - 10^{-3}$ molar) of the parent molecule the solvent contains sufficient supporting electrolyte to make it conductive. The supporting electrolyte usually has a large cation, such as found in the tetra-alkylammonium salts, to reduce ion pairing. It is obvious that the choice of solvent is critical since it represents the principle source of unwanted side reactions. Previous to this work acetonitrile, ³³ dimethylformamide, ³⁴ dimethyl sulfoxide, ³⁵ water.³⁶ and ethanol-water mixtures³⁷ have been used as solvents. These were chosen because they were obtainable in high purity and were relatively inert to the supporting electrolyte, the radical anion, and the parent molecule. Besides this they were capable of dissolving and dissociating a large enough amount of a supporting electrolyte to make the resulting solution conductive. In spite of these advantages there are two essential difficulties involved with all of the solvents thus far mentioned. First the solvents themselves are reducible at the high reduction potentials necessary to produce the more unstable radicals, and consequently the radicals themselves are never generated. Second the relatively high freezing point of all these solvents makes it impossible to cool the solutions much below room temperature. It has long been known from chemical reduction work that many radicals are stabilized by cooling and are observable only at low temperature.^{31,32} Thus although the technique of electrolytic reduction had many advantages of its own, it is lacking the two principle advantages of chemical reduction, namely a large reduction potential and the ability to cool the reducing solutions. It was the desire to combine the advantages of both the chemical and electrolytic methods that led us to examine the possibility of using liquid ammonia as an electrolytic solvent.

-11-

III. AMMONIA SYSTEMS

A. Metal Ammonia Solutions

It has long been known that liquid ammonia will dissolve certain metals (primarily the alkali and alkaline earth metals) to produce blue, paramagnetic solutions. Several reviews of these fascinating solutions have been written to which the reader is referred for a detailed discussion of their properties.³⁸⁻⁴¹ The discussion below is limited to a summary of the various theories about the nature of the reducing species present in these solutions.

One of the earliest models for the solution of a metal in ammonia was postulated by Kraus 42 who suggested that the solution reaction be represented by the equation

$$Metal_{solid} = M^+ + e^-$$

(13)

A started

where both the metallic cation (M^{\dagger}) and the electron (e^{-}) were solvated. This model was based upon the fact that the dilute solutions are extremely conductive and that the negative carrier transference number is about seven times that of the positive carrier, implying a very small mobile negative carrier.

Later measurements on bulk magnetic susceptibility⁴³ showed that the molar susceptibility decreased as the concentration of metal increased and indicated that a further reaction was necessary to account for the pairing

This model is still generally agreed to be correct for very dilute solutions, and Kraus's electrochemical dataare probably the only data available on these solutions that is universally accepted as being accurate.

-12-

of spins. A model proposed by Ogg^{44-45} postulated that the unpaired electron of Eq. (13) existed in a solvent cavity and that a pairing reaction

$$2e^{-} = e^{2^{-}}$$
 (14)

produced singlet electron pairs inside a solvent cavity.

A more recent model by Becker, Lindquist, and Alder⁴⁶ postulates four species in chemical equilibrium. The first two species are the metal ion and solvated electron of the earlier theories. In addition they postulate the existence of a "monomer", M, which consists of an alkali metal ion surrounded by approximately six oriented ammonia molecules with an electron circulating around the metal ion on the protons of the ammonia molecules. The concentration of this monomer is governed by the equilibrium reaction

$$M = M^{+} + e^{-}$$
(15)

Finally they postulate that two monomers can come together to form a singlet dimer, M_0 . The reaction for the formation of the dimer is

$$M + M = M_2$$
(16)

and is analogous to the formation of Na_2 in the gas phase. The fact that the paramagnetic species has something to do with the metal cation was confirmed by the NMR Knight shift measurements of McConnell and others.^{47,4}

Gold, Jolly, and Pitzer⁴⁹ have combined certain features of the Ogg and Becker models and have proposed still another model for these solutions. Their model retains the concept of an electron cavity and proposes that the monomer of the Becker model is simply an ion pair between the electron cavity and a metal cation. The diamagnetic species analogous to the Becker dimer is a quadrupolar assembly consisting of two ion pairs with the wave functions of the two electrons overlapping sufficiently to

produce a singlet ground state. This model was an attempt to explain certain spectral data ⁴⁹ indicating that the absorption spectra follow Beer's law and are independent of the alkali metal used.

From even a brief survey of the current literature it is obvious that none of these theories is conclusive and the issue is still open to considerable question. In order not to prejudice the argument in the following experimental description we shall follow the convention of Laitinen and Nyman⁵⁰ and refer to any and all paramagnetic species in these solutions by the single name "electron".

B. Electrolysis in Liquid Ammonia

Several workers have investigated the electrolysis of solutions of tetra-alkyl ammonium salts in liquid ammonia. Forbes and Norton⁵¹ measured the cathode potential for the reaction

$$NR_{l_{4}} = NR_{l_{4}}^{+} + e^{-}$$
 (17)

where R was one of several different alkyl groups. They found the cathode potential to be essentially independent of the alkyl group used and came to the conclusion that the actual cathode reaction was

e^(solvated) = e^(electrode) (18)

ALAN S. L. ADV

Laitinen and Nyman⁵⁰ studied the polarography of these salts in liquid ammonia at both mercury and platinum electrodes. They found that a polarographic wave with no limiting current occurred at essentially the same voltage for all the quarternary salts studied. They came to the conclusion that the only cathode reaction was a dissolution of electrons into the solution and they referred to this as the "electron electrode". Doyle⁵² studied the ESR spectrum of a frozen solution of electrolyzed

-14-

tetramethyl ammonium iodide in liquid ammonia and found that it was paramagnetic and that the ESR spectrum consisted of a single line with a width of 2.5 gauss. We have taken the ESR spectra of liquid solutions of electrolyzed tetramethyl ammonium iodide and found them to be similar to solutions of sodium in liquid ammonia (see below). These ESR experiments along with the polarographic data show rather conclusively that the reduced species in the tetra-alkyl ammonium salt solutions is similar to the reduced species in the alkali metal solutions.

C. Chemical Reactions in Liquid Ammonia

The production of radical anions by dissolving organic molecules in metal-ammonia solutions has long been postulated by organic chemists. Polymerization and hydrogen abstraction reactions involving unsaturated hydrocarbons have been assumed to proceed via a radical-anion mechanism, and this type of reaction has been thoroughly studied.^{53,54} In fact, in his original observation of the ESR spectrum of a radical anion²² Weissman compared the production of the anion in tetrahydrofuran with the solution of sodium in ammonia. A thorough review of organic chemistry in liquid ammonia has recently been written.⁵⁴ This review, which was brought to the author's attention after the experiments described below were completed, anticipates many of the results described below and suggests many possibilities for future research.

-15-

IV. EXPERIMENTAL TECHNIQUES

A. <u>Electrolysis Cell</u>

A photograph of the cell and Dewar in which the electrolysis was carried out is shown in Fig. 1 and a diagram of this equipment is shown in The platinum wire cathode is sealed into the lower tube by a Fig. 2. pressure glass-to-metal seal and made vacuum tight with epoxy resin cement. The lower tube, which is the only part of the cell that is placed in the microwave cavity, is made of quartz and is connected to the Pyrex part of the cell with a graded seal. The anode is contained in the inner tube and consists of a cylinder made of platinum foil and attached via a platinum wire to the tungsten wire that is sealed into the glass at the top of the cell. There is a hole in the inner tube above the level to the ammonia to allow easy cleaning of the anode compartment and to equalize the pressure throughout the cell. The anode and cathode compartments are separated by a glass frit to prevent the iodine produced at the anode from diffusing back into the cathode tube. The end of the lower tube is raised slightly from the bottom of the cell proper to prevent any solid supporting electrolyte from falling into the lower tube. The cell is connected to the vacuum line through a ball and socket joint and is held in place in its supporting Devar by the large standard taper joint. The overall length of the cell is roughly 30 cm. and the length of the lower tube is roughly 10 cm. When filled to the operating point the cell contains 5-10 ml. of solution.

Armstrong Products Company C-3 resin was used. Some care must be shown in the selection and application of these cements since certain cements are paramagnetic, and all cements are paramagnetic if insufficiently cured.

3 - N - S

1.13

¥



Fig. 1



Fig. 2

MU-33781

The electrolysis voltage was supplied by a voltage regulated power supply. A simple potentiometer circuit was used to vary the electrolysis voltage and either the voltage or current could be continuously monitored by a voltmeter connected either across the cell or across a 1000 ohn resistor which was in series with the cell.

-19-

B. Cooling System

When in use the cell is placed in the unsilvered quartz Dewar and the entire assembly is held rigid in the microwave cavity by a Teflon collet and aluminum collar fitting onto the stacks of the cavity. Since the ammonia solutions are quite lossy it is important that the sample tube be placed as nearly as possible in the node of the microwave electric field. With the platinum cathode approximately half way into the cavity a satisfactory loaded cavity Q was possible.

A transfer Dewar was connected to the lower standard taper of the sample Dewar via a ball joint elbow, and cold nitrogen gas was blown through the Dewar, past the cell, and out the top. The nitrogen gas was boiled from a reservoir of liquid nitrogen by means of an electric immersion heater, and the temperature of the cell was controlled by the amount of current passed through the heater. The temperature of the cell for a given heater power is of course a function of the heat loss in the specific! Dewar arrangement used. With the Dewars used in these experiments a power dissipation of approximately 32 watts in the heater would maintain the cathode at the freezing point of the solutions used (approximately -78° C.). When necessary the temperature of the cell. Quite large temperature gradients between the top and bottom of the cell were unavoidable but these did not prove inconvenient. Since the section of the Dewar inside the cavity must be unsilvered there was considerable heat loss, and dry air was blown through the cavity to prevent condensation of moisture. The temperature variation with this system was less than one degree over the time necessary to complete the measurement of a complete spectrum.

C. ESR Spectrometer

The ESR spectra were obtained on a conventional X-band reflection spectrometer employing 100 kc. magnetic field modulation and phase detection. With the exception of modifications mentioned below the spectrometer has been previously described.⁵⁵ The DC magnetic field was provided by a Pacific Electric Motors twelve inch electromagnet driven by a current stabilized power supply. The field homogeneity and power supply stability were such that there was less than a .001% field variation over a cylinder volume one inch in diameter. Of course, the effective sample volume in the cavity was much less than this, and field homogeneity over the sample was correspondingly higher. The magnetic field was slowly swept by a Hewlett-Packard low frequency function generator which was modified so that sweeps as slow as 2 hrs. per cycle (1 hr. per sweep) could be obtained with no sacrifice in linearity. The sample was contained in a Varian rectangular cavity, Model V-4531, operating in the TE₀₁₂ mode with a loaded resonance frequency of approximately 9.2 gc.

Magnetic field intensity measurements were made with a marginal proton oscillator using a water sample doped with 0.1 \underline{M} copper ion. To prevent instability caused by mechanical vibration, a rigid coaxial line was used between the oscillator and the sample coil, and the oscillator was remotely tuned by varying the bias voltage on a varactor diode in the oscillator tank circuit. The diode was thermally insulated to prevent instability and the bias voltage was provided by mercury cells. The

-20-

position of a given line was measured by adjusting the magnetic field until it was in the middle of the line, tuning the NMR oscillator to the middle of the proton resonance, and counting the oscillator frequency on a Hewlett-Packard frequency counter. The oscillator was stable to several parts in 10^7 over the period of time necessary to make a single measurement and was consequently never a major source of error. The principle source of error in measuring the position of a given line was in determining exactly the middle of the line.

-21-

In making g value measurements the microwave frequency was measured with a Hewlett-Packard transfer oscillator and frequency counter.

D. Typical Procedure

At the start of each run a small amount of supporting electrolyte was placed in the cell. When tetramethylammonium iodide was used enough was placed in the cell to produce a saturated solution (0.0023 M at -78° C.). With the other salts used a saturated solution was probably obtained. At this point the cell was connected to the vacuum system and thoroughly evacuated. A calibrated volume was filled to a known pressure with sample, and the cell was cooled almost to liquid nitrogen temperature. At this point the vacuum system was sealed off from the pumps and the sample was allowed to distill over into the cell. The progress of the distillation could be followed by monitoring the pressure on a thermocouple gauge attached to the vacuum system. When a non-volatile sample was involved it was placed directly in the cell before evacuation. After the distillation was complete a small amount of ammonia was distilled into the cell, the cell was warmed to somewhere below the freezing point of ammonia, and the rest of the ammonia was distilled in. It was found that if the ammonia was distilled into the cell at liquid nitrogen

temperatures, it tended to crack the lower tube. After enough ammonia had been distilled over to cover the platinum anode, the cooling was shut off, the cell was allowed to warm, and the solution was stirred by the bubbles evolving from the bottom of the lower tube. When the solution had been thoroughly stirred the cell was again cooled so that the temperature of the lower tip was just above the freezing point of the solution. The freezing and thawing could be followed both by monitoring the current through the cell and by observing the change in cavity Q and frequency produced when the sample froze. After the cell was filled the system was allowed to sit until it had reached thermal equilibrium (approximately 20 minutes) and the cavity resonance frequency had stopped drifting.

The optimum electrolysis voltage varied with the concentration and nature of the sample used. To obtain the best signal-to-noise ratio the highest possible voltage was used to produce the highest steady state concentration of radicals. However at too high a voltage there are two mechanisms which tend to again decrease the signal-to-noise ratio. First the "electron" line which appears tends to overlap and obscure the radical spectrum. Second the higher concentration of electrons produces the diamagnetic dianion and reduces the radical concentration by the following reaction.

$$R^{-}(paramagnetic) + e^{-} = R^{2-}(diamagnetic)$$
 (19)

1.101

A typical example of voltage and concentration would be a solution 0.005 \underline{M} in butadiene electrolyzed at a potential of -25 volts.

Because the radicals examined by this technique are unstable some care must be used to optimize the experimental conditions. Extremely small steady state radical concentrations are generated under the best of circumstances and it takes very little reactive impurity to reduce

-22-

these concentrations to the point where no signal is observed. Therefore all glassware must be scrupulously clean and the ammonia and supporting electrolyte must be of very high purity. After acquiring an experimental technique the experiments on a given molecule under a given set of experimental circumstances became quite reproducible. However the optimum conditions varied widely from molecule to molecule and a good bit of trial and error was necessary in order to achieve the best signal-to-noise ratio. The choice of supporting electrolyte seemed to be particularly critical. With butadiene the spectrum is almost unobservable when using sodium iodide although a very good signal-to-noise ratio could be obtained using tetramethylammonium iodide. With most of these radicals we were operating at the limits of the spectrometer's sensitivity and consequently these considerations determine not simply the quality of the spectrum but whether or not one sees any signal at all.

-23-

E. Chemicals

The tetramethyl-, tetraethyl-, and tetrabutylammonium iodides were Southwestern Analytical Chemicals polarographic grade. They were stored continuously <u>in vacuo</u> over magnesium perchlorate and were used without further purification. Some Eastman White Label tetramethylamnonium iodide was also used. It was recrystallized from a four to one ethanolwater mixture and also stored <u>in vacuo</u>. The tetra-n-propylammonium perchlorate was made by titrating a 10% aqueous solution of Eastman tetra-n-propylammonium hydroxide with Baker and Adamson perchloric acid. The water insoluble salt was thoroughly washed with cold water and dried <u>in vacuo</u>. Baker and Adamson sodium iodide was dried at 110°C. and used without further purification. Matheson reagent grade ammonia was used without purification. This grade is quoted as having a minimum purity of 99.99% and in the author's experience this is probably fairly accurate. The dimethyl ether used was Matheson research grade and when it was used as a mixed solvent sufficient sodium metal was added to the solution to produce the bronze metallic sodium-ammonia phase. The mixture was allowed to sit in contact with the sodium overnight and was degassed before being distilled into the electrolysis cell.

The deuterated cycloheptatriene was prepared in the following manner. Equimolar portions of cycloheptatriene and triphenyl methyl bromide were allowed to react in a liquid SO₂ solution at approximately -17°C. After the reaction was complete the solvent was removed by vacuum distillation. The cycloheptatrienyl bromide produced was dissolved in dimethyl ether and allowed to react overnight at dry ice temperature with lithium aluminum deuteride. The product was distilled off and purified by bulb to bulb distillation on the vacuum line. A vapor phase chromatogram of the product showed only one peak with the same retention time as the undeuterated material. An NMR spectrum of the deuterated material matched that reported by Jensen and Smith⁵⁶ for 7-deuterocycloheptatriene.

The sources of other chemicals used are listed below. The volatile samples were purified by bulb to bulb distillation on the vacuum line and all others were used without further purification.

Butadiene - Phillips Petroleum Company Research Grade

Isoprene - Phillips Petroleum Company Research Grade

The author is indebted to Miss Carolyn Talcott for carrying out the synthesis of the deuterated cycloheptatriene, and to Professor F. R. Jensen for suggesting the method.

-24-

Cyclohexadiene - Matheson, Coleman, and Bell Technical Grade

2,3 dimethyl butadiene - Matheson, Coleman, and Bell Practical Grade Nitrobenzene - Eastman Organic Chemicals, White Label

Nitrosobenzene - Aldrich Chemicals

Hexatriene - Aldrich Chemicals

Cyclooctatetraene - Aldrich Chemicals

Cycloheptatriene - Prepared by Professor F. R. Jensen's research

group.

The author would like to thank Professor Jensen and his group for the sample of cycloheptatriene.

V. RESULTS AND DISCUSSION

A. Butadiene

The ESR spectrum of the butadiene radical anion was obtained by electrolyzing a 5 X 10^{-3} <u>M</u> solution of butadiene in liquid ammonia at -78°C. The solution was saturated with tetramethylammonium iodide.^{*} The spectrum obtained and the numbering of the atoms is shown in Fig. 3.

The spectrum is seen to consist of five groups of three lines each. If the two protons attached to the end carbon atoms are equivalent then only two proton coupling constants could be expected. Since the coupling constant A_1 (= A_4) is greater than A_2 (= A_3) then one would expect five sets of triplets as is experimentally observed.

The spectrum was measured several times over a range of microwave power and field modulations and the coupling constants in Table I were obtained. The difference in field between Lines 1 and 2 were the same as between Lines 1⁴ and 15 thus showing that second order terms in the spin Hamiltonian could be neglected. The field difference between the points of maximum slope of the center line at -78° C. is 0.3 gauss.

The ESR spectrum of this solution without the butadiene consisted of a single very intense line of 0.21 gauss halfwidth. The g value of the line was 2.0007. When the electrolysis voltage was turned off the electron line slowly decayed following a zero order rate law.

-26-


MU-32841



	erved bata for 1,5-butaurene	
A =	7.617 ± 0.005	gauss
A ₂ =	2.791 ± 0.007	gauss
Q(Av.) =	20.82 ± 0.02	gauss
Linewidth =	0.37	gauss
g =	2.0024	

m.

Using these values and assuming a Lorentzian lineshape a theoretical spectrum was calculated. This calculation was performed on an IBM 7094 Computer and the results were plotted on a California Computer Company digital x-y plotter. The plot is shown in Fig. 4 and as can be seen the agreement between the observed and calculated spectrum is excellent. Details of the calculation are given in Appendix I.

The line width of the spectrum was not found to vary with temperature within our experimental accuracy between -78° and -68°C. The lifetime of the radical anion was determined by measuring the decay of the signal after the removal of the electrolysis current. At -78°C. the decay was found to follow first-order kinetics with a half-life of 2 sec. Since the signal-to-noise ratio depends greatly upon the experimental conditions, this implies that the half-life probably depends upon the temperature and solute. We have no indication that the observed line width is due to electron exchange with neutral butadiene, but it is possible that solute concentration or other factors may be the primary source of line width. Unlike conventional solvents, in this medium chemical exchange with the solvent itself is possible and may be responsible for these rather wide It has been shown that an exchange mechanism of this sort can lines. effect the apparent values of the coupling constants.⁹¹ However, calculations performed on the butadiene radical anion show that the maximum effect in this radical would be approximately the same as the experimental uncertainty in the coupling constant measurements. 92 Magnetic field inhomogeniety was not a source of line width.

The molecule 1,3-butadiene has been considered ^{57,58} as a model system for pi-electron molecular orbital calculations. The observed values of the proton coupling constants can be related to theoretical

-29-



MUB-2276



spin densities with Eq. (7) if the Q values are known. Recent evidence¹⁶ indicates that the Q for every carbon position must be calculated taking into account a variation of Q with charge density. In our case since we know the proton coupling constant for every carbon atom an average Q value can be exactly determined. Thus by symmetry, we know that

$$\rho_1 + \rho_2 = 0.5 \tag{20}$$

and so

$$Q(A_V) = 2(A_1 + A_2) = 20.82 \text{ gauss}$$
 (21)

This value is particularly small and is therefore consistent with Eq. (9) where Q in radical anions should decrease with the charge density. If one also considers the values of $Q(C_{0}H_{0}^{-}) = 25.67^{59}$ and $Q(C_{0}H_{0}^{-}) = 22.50$,³¹ there appears to be a nearly linear decrease of Q with charge density. The three radical anion Q values indicate that in Eq. (9), K should be close to 40 and Q around 30.0 gauss while Colpa and Bolton¹⁶ obtained K = 17 and $Q_{0} = 31.2$ gauss from other data. It is quite possible that changes in the hybridization of the C-H orbitals are partly responsible for these low values of Q. The trend with charge density is moderately close to that expected from Colpa and Bolton's equation, but a rather large K value must be assumed.

Giacometti <u>et al</u>.¹⁷ have obtained satisfactory agreement for the radical ions considered by Colpa and Bolton and for $C_{6}H_{6}$. In the later case agreement was only obtained if overlap was included in the usual Huckel treatment. If we apply the equations recommended by Giacometti <u>et al</u>. to the usual Huckel orbitals⁶⁰ for butadiene radical anion, the

predicted proton coupling constants are $A_1 = 9.8$ gauss and $A_2 = 3.8$ gauss. These values are essentially unchanged by the inclusion of overlap as recommended by Giacometti <u>et al</u>. These coupling constants are both about 25% larger than the observed ones, and it does not seem that this treatment has any advantage over that of Colpa and Bolton even if overlap is included.

If we neglect the variation of Q with charge density, a direct comparison of the experimental value of A_1/A_2 with theoretical values of ρ_1/ρ_2 can be made. In Table II such a comparison is given for a series of one-electron molecular orbital wave functions. It can be seen that simple Huckel theory gives a most satisfactory agreement.

The inclusion of d-orbitals by Sover and Kauzman⁶¹ is an interesting extension of Huckel theory. The d-orbital value in Table II is the sum of p and d-electron spin densities. Since the Q values would not be expected to be identical for these two kinds of orbitals, the spin density ratio shown in Table II is of only qualitative significance. The three SCF values fall far short of the mark and a considerable improvement must be made in this theory to approach Huckel theory for spin density calculations.^{*}

Some interesting valence bond structures can be drawn for our radical anion as follows:

$$\begin{array}{c} \Theta^{\bullet\bullet}_{C-C-C=C} & \text{Ia} \\ \Theta^{\bullet\bullet}_{C-C=C-C} & \text{Ib} \end{array}$$

^{*} Hayes ⁶² has performed a SCF calculation on the 5 electron pi system for the butadiene radical anion and gotten 3.39 and 2.97 as values for the ratio ρ_1/ρ_2 for the cis and trans isomer respectively. The author does not know the details of this calculation.

Table II. Comparison with Theory

$A_{1}/A_{2} $ (expt.) = 2.729 ±	0.007
ρ_1/ρ_2 (cal.)	Theory
2.615	Simple Huckel Theory
2.219	Huckel Theory with variable β
2.9	Huckel Theory with d-orbital ^a
1.9	SCF (without net charge) ^b
1.6	SCF (with net charge) ^C
2.97	SCF (with net charge) ^d
^a Ref. 17 ^b Ref. 1	
^c L. Goodman by private communication ^d Ref. 62	

ĺ,

Structures Ia and Ib are those of a substituted allyl radical and simple valence bond arguments would predict that $\rho_1/\rho_2 = 2$. Since structures of the type II do not place the odd electron at all on the middle carbon atoms, the inclusion of these structures can only increase ρ_1/ρ_2 . Since simple resonance considerations would give a greater importance to the structures of Type I, one would predict that $\rho_1/\rho_2 > 2$ and it should not be too far above the lower limit. The valence bond structures also predict that the negative charge should be even more concentrated on the end carbon atoms than is the spin.

The simple Huckel theory can also be modified for the fact that the radical anion should have two β values.⁶⁰ Since the bond between the middle carbon atoms is the longer one it should also have the smaller resonance integral. The assumption that β is proportional to the overlap integral S will lead to this type of variation. The bond length data of Almenningen <u>et al</u>.⁸⁷ and the overlap integrals of Mulliken <u>et al</u>.⁷⁰ lead to values of 0.9 and 1.1 for the values of the resonance integrals of the end and middle carbon-carbon bonds respectively. We have performed a Huckel calculation using these matrix elements and have found that this calculation gives a value of $\rho_1/\rho_2 = 2.219$. This modification is in the wrong direction to compensate for a correction based upon the variation of Q with spin density where we expect that $Q_1 < Q_2$, but at the present time there is considerable undertainty about the variation of Q with either charge density or spin density.

Ċ-[⊖]Ċ-C=C

-34-

B. Methyl and Methylene Coupling Constants

As we have seen the hyperfine splittings due to protons attached to pi-bonded carbon atoms can be analyzed theoretically by simple and straightforward means (e.g. Eqs. (7 & 9)). However splittings due to protons attached to aliphatic substituents such as methyl or methylene^{*} groups involve some additional theoretical considerations. There are two problems that arise when one considers aliphatic substituents. The first is a question as to how any unpaired spin density gets into the aliphatic group. The second is that, given a mechanism for getting unpaired spin density into the aliphatic group, how does one then calculate the hyperfine coupling constants from a knowledge of this spin density distribution.

The model most recently used with considerable $\operatorname{success}^{63,64}$ to account for methyl hyperfine splittings is that of hyperconjugation with the methyl group itself. This model mixes the pi molecular orbitals of the conjugated system with orbitals of the correct symmetry centered on the methyl group and this extends the conjugated system. The result is a flow of electrons between the methyl group and the unsaturated part of the molecule and a net unpaired spin density on the methyl group. An alternate model is that of spin exchange polarization similar to that used by McConnell¹³ to explain the production of unpaired spin density at the hydrogen nuclei in the plane of a pi-radical. In this model the unpaired pi-electron remains in the unsaturated part of the molecule but produces unpaired spin density at the methyl protons via polarization of

* Of course we are here referring to sp^3 bonded methylene carbons and not to sp^2 carbons which are a part of the pi-system such as in butadiene.

-35-

the sigma electrons in the C-H methyl bond. This polarization may be either direct or through a polarization of the sigma electrons in the carbon-carbon bond. In this section we shall assume that the principle mechanism for methyl and methylene coupling constants is hyperconjugation, and that the effects of spin polarization may be accounted for by a small correction term. In the next section we shall provide some justification for this assumption and shall derive the correction term from experiments on cycloheptatriene.

As was mentioned in the last section, the simple Huckel molecular orbital treatment of conjugated systems has been remarkably successful in interpreting the ESR spectra of alternate hydrocarbons. This theory has been explained quite simply by Streitweiser^{60} whose notation we will use in the following discussion. Because of the success of this method it is desirable to attempt to include the hyperconjugation model within the general Huckel framework. This was first done by Mulliken et al. in the following manner. They assumed that the 1s atomic orbitals of the hydrogens could be combined in some manner to produce a pseudo atomic orbital, Z, which was centered on the hydrogens and was of the correct symmetry to combine with the $2p_{\tau}$ atomic orbitals of the unsaturated carbon system. The $\rm H_2$ pseudo-atom was then considred as a part of the methyl group was attached. Thus by assuming off-diagonal matrix elements connecting C' with C and C with H_3 , and on-diagonal elements for C and ${\rm H_2}$ the hyperconjugating methyl group could be included in the usual Huckel calculation.

It was pointed out by Coulson and Crawford⁶⁶ that because the C-H₃ bond was so short, the assumption that $S_{i,j} = \delta_{i,j} \begin{pmatrix} \delta_{i,j} \end{pmatrix}$ is the Kronecker

-36-

delta), usually made in the Huckel approximation, is no longer valid and that the calculation should be carried out using the complete overlap matrix, \tilde{S} . They made the assumption that the off-diagonal S and H matrix elements were proportional to each other and that both were proportional to bond length. With the S and H values thus derived and with some fairly arbitrary values for the on-diagonal H matrix elements they performed a series of calculations.

Bolton and co-workers⁶³ modified Coulson's method in an attempt to be able to include the effects of non-vanishing overlap elements in the methyl group without adding the additional computational difficulties that are encountered when overlap is included for the entire pi-system. They formed two molecular orbitals for the methyl group by combining the atomic orbitals on C and H_3 using overlap and the parameters of Coulson and Crawford. This of course involved only two by two matrices and was a fairly simple calculation even including overlap. It turned out that the resulting anti-bonding molecular orbital was so high in energy that they felt it could be neglected. This meant that the methyl group could be treated as a heteroatom where the bonding molecular orbital now became the pseudo atomic orbital. The previous calculation provided the matrix elements connecting it to the unsaturated system, and the usual Huckel calculation could be performed with neglect of overlap since the overlap of the methyl group had already been included.

Colpa and deBoer⁶⁴ examined the absolute magnitudes of the coupling constants predicted by the theory of Bolton <u>et al</u> and came to the conclusion that the neglect of the anti-bonding molecular orbital was unjustified since it led to values of the coupling constants which were considerably lower than those observed experimentally. Their contention

-37-

was that the only reasonable way to treat the hyperconjugation model was to perform the full overlap calculation of Coulson and Crawford. The calculation starts with the matrix eigenvalue equation

$$\widetilde{HC} = \widetilde{SCE}$$
(22)

Following the method of Lowdin 67 we can rearrange Eq. (22) to the following form

$$H'C' = C'E$$
 (23)

where

$$H' = S^{-\frac{1}{2}} H S^{-\frac{1}{2}}$$
(24)

and

$$C = S^{-\frac{1}{2}}C'$$
 (25)

Thus the problem is reduced to the usual Huckel form and the transformation $S^{-\frac{1}{2}}$ can be used to transform the resulting eigenvector matrix C! into the molecular eigenvector matrix C. The matrix $S^{-\frac{1}{2}}$ may either be computed from the series expansion as was done by Lowdin or by application of a quite general theorem.⁶⁸ The theorem states that for any matrix A which can be diagonalized by a transformation, T, according to the following equation,

$$T^{-1}AT = A_{D}$$
 (26)

(27)

(28)

1

any function f(A) is given by

$$Tf(A_D)T^{-1} = f(A)$$

where

$$(f(A_D))_{aa} = f((A_D)_{aa})$$

for all values of a.

In spite of the success of simple Huckel theory there are certain effects which it cannot explain. The principle effect is that of negative spin density in which the closed shell pi-electrons are polarized by the odd electron to produce a net negative spin density at points in the molecule where the unpaired electron wave function is small or vanishing. This correlation effect arises from the electron-electron repulsion term in the molecular Hamiltonian which is neglected completely by Huckel theory. In order to account for negative spin density and other electron correlation effects McLachlan⁶⁹ proposed an approximate self-consistent field theory which took electron correlation into account in a simple and straightforward manner. His theory led to the following formula for the spin density:

$$\rho_{r} = C_{ro}^{2} - \lambda \Sigma \Pi_{rs} C_{so}^{2}$$
(29)

where C_{ro} is the Huckel coefficient of the odd orbital on atoms r, Π_{rs} is the mutual polarizability of atoms r and s, and λ is a constant derived from the theory to be about equal to 1. We have combined the theory of McLachlan with the hyperconjugation model of Mulliken⁶⁵ in an attempt to account for correlation effects in the methyl group.

Once one has calculated the electronic wave function with one of the above methods there still remains the problem of calculating the hyperfine coupling constant for comparison with experiment. Colpa and deBoer⁶⁴ have touched briefly on this problem but their treatment is sketchy and the method they used to obtain their results is not obvious. We have extended their treatment to provide a specific formula for the coupling constants of methyl and methylene protons.

We first consider the case of methylene protons. The methylene

-39-

group consists of one hydrogen atom above the nodal plane of the pi-system and one hydrogen atom below the nodal plane. If we denote the normalized ls atomic orbitals centered on these two atoms as ϕ_{ls}^{U} and ϕ_{ls}^{L} respectively we can combine them to form one pseudo atomic orbital of the correct symmetry to combine with the pi-orbitals of the rest of the molecule. This pseudo atomic orbital is

$$\Pi_{\rm H} = \mathbb{N}(\phi_{\rm ls}^{\rm U} - \phi_{\rm ls}^{\rm L}) \tag{30}$$

where the normalization constant N is given by

$$N = \frac{1}{\sqrt{2(1-S_{UL})}} = .834$$
(31)

The overlap integral S_{UL} is taken from the tables of overlap integrals of Mulliken <u>et al</u>.⁷⁰ and assumes the bond lengths and angles shown in Fig. 5.

In the LCAO approximation the molecular orbital in which the unpaired electron moves is given by

$$\Psi_{o} = \sum_{i} C_{oi} \Psi_{i}$$
(32)

where the Ψ 's are the atomic orbitals including the $2p_z$ orbitals on each of the carbons and the pseudo atomic orbital Π_H on the hydrogens. Then the spin density at either of the methylene protons is given by

$$\rho(\rho) = \sum_{l,m} C_{o\ell} C_{om} \Psi_{\ell}(\rho) \Psi_{m}(\rho)$$
(33)

in the case where overlap is included or by

$$\rho(\rho) = \sum_{l} c_{ol}^{2} \Psi_{l}(\rho)^{2}$$





where the assumption of zero differential overlap is made. Using the atomic orbitals listed in Table III an expression for the total spin density at the proton can be evaluated. In order to convert this to a coupling constant one must multiply the total spin density by

$$\frac{A_{\text{Hydrogen Atom}}}{[\phi_{1s}(p)]^2} = \frac{508 \text{ gauss}}{2.161} = 235.1$$
(35)

The only important terms in the series expressions given by Eqs. (33 & 3⁴) are those evolving the coefficients of the pseudo orbital (C_H) , the methylene carbon (C_C) , and the two carbons to which the methylene is attached $(C_C, \text{ and } C_{C''})$. Of these terms the C_C^2 and $C_{C''}^2$ terms are also negligible. The resulting expression for methylene coupling constants is given by

$$A_{\text{methylene}} = 327C_{\text{H}}^{2} + 19.8C_{\text{C}}^{2} + 161C_{\text{C}}C_{\text{H}}$$
$$+ (5.95C_{\text{H}} + 1.46C_{\text{C}})(C_{\text{C}}, + C_{\text{C}}'') \text{ gauss} (36)$$

If overlap has been neglected only the first two terms of this expression need be used.

The theory of methyl group coupling constants is similar to that of methylene except that the lack of symmetry with respect to the nodal plane of the pi system complicates things somewhat. These complications have been worked out quite explicitly by Chesnut⁷¹ who has accounted for the chemical equivalence of the methyl protons by averaging over various static configurations of the methyl group. We have used Chesnut's method to provide a formula for evaluating methyl group coupling constants from a knowledge of spin distribution. Our values for the significant Γ matrix elements (defined in Ref. 71) are given in Table IV and the formula to

Table III. Atomic Orbitals.

-43-

which they lead is

$$A_{\text{methyl}} = 219.8 C_{\text{H}}^2 + 13.17 C_{\text{C}}^2 + 107.7 C_{\text{H}}^2 C_{\text{C}} + 3.997 C_{\text{H}}^2 C_{\text{C}}$$

+ $0.973C_{C}C_{C}$, gauss

- (37)

(38)

Here again if overlap is neglected only the first two terms need be considered.

In order to test the above theories several methyl or methylene containing radical anions were prepared and their ESR spectra measured. The radical anion of 2,3-dimethyl 1,3-butadiene was prepared by electrolysis of a 0.01 M solution of the parent hydrocarbon dissolved in a solution of liquid ammonia saturated with tetramethylammonium iodide. At low voltages (e.g. 10 volts) the spectrum consisted of five septets of rather wide lines. As the voltage was raised (e.g. 30 volts) the lines narrowed and the lines of the inner septets were further split to give the spectrum shown in Fig. 6. If the voltage was raised even further (e.g. 100 volts) the line width remained roughly constant but the spectrum became considerably weaker. If the voltage were at this point reduced to the intermediate level the spectrum would grow very rapidly and then decay to the level it originally had when the voltage was at an intermediate (e.g. 30 volt) level. We interpret this behavior as evidence for the formation of a relatively stable diamagnetic dianion which is in equilibrium with the electron and the radical anion according to the following equation:

 $R^{2-} = R^{-} + e^{-}$

As the voltage is raised the production of excess electrons shifts the equilibrium to the left and causes the radical anion concentration to

-44-





decrease and the steady state dianion concentration to increase to quite a high level. When the voltage is again reduced the production of electrons is decreased, the steady state concentration of electrons drops, and the equilibrium shifts rapidly to the right. The initial high concentration of the dianion represents an excellent reducing agent and a high concentration of the radical anion results via the equilibrium

$$R^{2-} + R = 2R^{-}$$
 (39)

(40)

Eventually the supply of excess of dianion is exhausted and the concentration of the radical anion is governed by the equilibrium

$$R + e = R$$

and drops to its original value.

The line width versus electrolysis voltage characteristics of this system raise some interesting questions as to the source of line width in this radical. Unlike butadiene and most other radicals investigated, the source of line width in fairly concentrated solutions (0.01 M) appears to be due to an electron exchange relaxation mechanism between the radical and the neutral parent molecule similar to that occurring in more conventional solvents. The effect of increasing the voltage is to lower the concentration of the neutral molecule in the immediate vicinity of the electrode ^{*} via equilibria 38-40. When the neutral species concentration is decreased the line width also decreases. Just why the mechanism that produces the relatively karge line widths in most other species does not

In most of these radicals the lifetimes are so short that they can diffuse only a very short distance from the electrode before being destroyed. Consequently the ESR spectrum is a measure of conditions in the immediate vicinity of the gathode. operate here is open to question. If the principal source of line width in ammonia solutions is electron exchange with the solvent or the solute cation, it may be that the effect of the methyl groups in this molecule is to sterically block the approach of solvent or solute molecules and thus inhibit this source of relaxation.

The fact that the linewidth of dimethylbutadiene is far narrower than that of any other radical we have observed in ammonia solution is at least not inconsistent with such a theory.

A spectrum consisting of five septets could be readily assigned to the splittings caused by four equivalent methylene protons and six equivalent methyl protons. However the additional small splittings of the inner septets can only be accounted for by assuming a slight inequivalence of the methylene protons which produces two sets of two equivalent protons. On that basis the spectrum can be completely assigned with the coupling constants given in Table V. The theoretical spectrum calculated from these coupling constants is shown in Fig. 7.

The usual treatments for hyperfine coupling constants as given in Eqs. (7 & 9) predict a single pi-sigma interaction parameter for any given carbon and consequently imply that all protons attached to a given carbon should have the same coupling constant even if they are geometrically unequivalent. This conclusion is generally true and only one other case of unequivalent protons attached to the same carbon has been reported. Fessendon and Schuler⁷² have noted that the two methylene proton coupling constants in the allyl radical differ by 0.10 gauss. In order to explain this phenomenon an extension of the usual treatments of sigma-pi interaction is necessary.

Observed Data for 2,3-Dimethylbutadiene Table V.

	$A_{1} = 7.033 \pm 0.003$	gauss	
	$A_{1}' = 7.241 \pm 0.003$	gauss	
	$A_2 = 1.200 \pm 0.002$	gauss	
	Linewidth = 0.099	gauss	
	g = 2.0020	· · ·	
see	Fig. 12 for numbering		

Inasmuch as the 2p -atomic orbitals of carbon are invariant to any arbitrary rotation about an axis normal to the molecular plane, no molecular orbital scheme involving only these 2p,-orbitals as basis functions can explain the observed difference. The most straightforward expansion of the basis set to include functions of the appropriate symmetry would be to include the carbon atomic d orbitals as was done by Sovers and Kauzmann. They considered only the effect of the d orbitals on the electron distribution in the pi-system itself and neglected their effect on the pi-signa interactions. Thus their calculations cannot explain the different coupling constants but can serve as the starting point for further calculations of the effect of d orbitals on the sigma system.

It can be shown⁶¹ that of the five d-orbitals only two, the d_{xz} and $d_{_{_{VZ}}}$, are of the correct symmetry to combine with the $2p_z$ -orbitals. Thus the molecular orbital in which the odd electron moves can be expressed as $\Psi_{o} = \sum_{i=1}^{N} \left[C_{oi} \phi_{p_{z}}^{i} + C_{oi}^{i} \phi_{d_{yz}}^{i} + C_{oi}^{u} \phi_{d_{xz}}^{i} \right]$

(41)



Fig. 7

By considering only the CH_2 fragment composed of carbon atom j and two hydrogens it is clear that there exists a coordinate system such that either $\phi_{d_{yz}}^{j}$ or $\phi_{d_{xz}}^{j}$ vanishes. This is of course equivalent to transforming the coefficients C' and C" from the arbitrary coordinate system in which they were originally defined to a new coordinate system which in general is not the same as the coordinate system defined by the two C-H bonds. This produces the anisotropy which can account for the different coupling constants.

Using Sovers and Kauzmann's values for the coefficients of the d orbitals of butadiene, the principle d axis system is rotated from the bond axis system by approximately 3°. Myers⁷³ has shown that by making certain reasonable assumptions the 3° anisotropy would produce a difference in coupling constants on the order of 0.05 gauss in butadiene. This difference would have been too small to even produce a measurable line intensity anomoly with the limited resolution we were able to achieve with butadiene.

There are two mechanisms which could account for the larger anisotropies in dimethylbutadiene. First of all the methyl groups, through a hyperconjugation or inductive effect, will distort the pi system and alter the d orbital coefficients. By this mechanism the principal axis system of the d orbitals might be further shifted from the bond axis system. The second mechanism which might be important would be the steric effect of the methyl groups. This steric effect would tend to distort the molecular geometry itself and thus produce further anisotropy. The first effect might be looked upon as a shifting of the d orbital principal axis system, and the second effect might be looked upon as a shifting of the bond axis syst system. Since the total anisotropy depends upon the difference between

-50-

these two either could produce the observed effect. Unfortunately all of the usual techniques for measuring bond angles and distances give very little information about carbon hydrogen bond angles, and the second effect would be difficult to measure with the methods now available. Calculations are in progress to determine the magnitude of the first mechanism in dimethylbutadiene and to see how large a geometric distortion would be necessary to account for the observed differences.

The radical anion of 1,3-cyclohexadiene was prepared by electrolyzing a 3-millimolar solution of cyclohexadiene in liquid ammonia. The solution was saturated with tetramethylammonium iodide. In this case the optimum signal-to-noise ratio was produced with a rather high electrolysis voltage (ca. 60 volts). The resulting spectrum with the electron superimposed is shown in Fig. 8. At first sight the spectrum appears quite complex but the assignment is aided by the fact that only three distinct coupling constants are involved. The total width of the spectrum imposes the constraint that

Total width =
$$\sum_{n=1}^{N} I_n A_n$$
 (42)

where I_n and A_n are the spin and coupling constant of the nth magnetic nucleus respectively. This constraint allows one to determine the 3rd coupling constant if the first two are known so the problem of assigning the spectrum is really a two parameter problem. The outermost triplet indicates that one of the coupling constants is given by the spacing of the lines in the triplet and a not unreasonablé guess for a second coupling constant would be the distance between the first and fourth lines. The coupling constants derived from this assignment are given in Table VI and the theoretical spectrum calculated from them and shown in Fig. 9

-'51-

Table VI. Observed Data for Cyclohexadiene

- 54-

 $A_1 = 1.996 \pm 0.009$ gauss $A_2 = 8.212 \pm 0.011$ gauss $A_3 = 11.114 \pm 0.012$ gauss Linewidth = 0.233 gauss g = 2.0025

See Fig. 12 for numbering

is seen to agree with the experimental spectrum.

The radical anion of isoprene was prepared by electrolyzing a 0.01 M solution of the parent molecule in liquid ammonia. Enough tetraethylammonium iodide was added to produce a saturated solution. Since tetraethyl ammonium iodide is much more soluble in liquid ammonia than the tetramethyl salt, the resulting saturated solution is more conductive. The best spectrum shown in Fig. 10 was produced at rather high electrolysis voltages (ca. 80 volts). At these voltages a large electron line is superimposed upon the isoprene spectrum. By lowering the electrolysis voltage the electron line could be eliminated and this did not change the radical anion spectrum.

Unfortunately in this case the assignment of the spectrum is not a trivial matter. Assuming that the protons on any given methyl or methylene group are equivalent or almost equivalent the spectrum should be able to be assigned with four coupling constants. After considerable effort to assign the spectrum by the usual intuitive method an attempt was made at a systematic approach to the problem. To begin with it is clear from the

1

1.1.1





spin Hamiltonian that in general every distinct coupling constant in any given radical is represented by the distance between the outermost line in the spectrum and one of the interior lines. The constraint imposed by Eq. (42) places an upper limit on the value of the largest coupling constant. In the case of isoprene this limit requires the largest coupling constant to be represented by the distance between the outermost line and one of the interior lines up to and including line number 23. Thus the four coupling constants must be chosen from the set of 22 numbers given by the positions of the lines 2 through 23 (defining the position of line 1 as zero). This limits the number of possible assignments to around 10^5 and the problem of checking each of them (with the aid of a computer) becomes tractable.

Most of the combinations are ruled out because they do not satisfy Eq. (42). Each of the 10^5 combinations were checked and only those which produced a total spectrum width within the range (experimental width \pm R) were saved. With R = 2% of the experimental width there were 208 combinations that satisfied this criterion. Seven specific critical lines were chosen in the experimental spectrum and each of the 208 remaining combinations were tested to see if they would predict a line at each of the seven experimental positions \pm R'. With R' = 1% of the total spectrum width only three combinations satisfied this criterion. The complete spectrum predicted by each of these three combinations was calculated and none of them agreed with the experimental spectrum. Thus within the accuracy of the experimental data there was no possible assignment of four coupling constants that would predict all the lines in the spectrum.

The cause of the difficulty is lines 4 and 5 indicated by arrows in Fig. 10. If the existence of these lines is ignored a very good

- 56-

assignment can be made for the rest of the spectrum with the coupling constants listed in Table VII. The theoretical spectrum based on these coupling constants is shown in Fig. 11 and may be seen to be in excellent agreement with the rest of the experimental spectrum. This excellent fit and the fact that the assignment agrees so well with the predictions of molecular orbital theory (see below) have led us to the conclusion that lines four and five are anomalous, perhaps caused by impurities, and that the assignment given in Table VII: is indeed correct.

We have performed a series of calculations on the three molecules mentioned above and on several other molecules containing methyl or methylene groups for which experimental data exists in the literature. For each molecule we have done a simple Huckel hyperconjugation calculation both including and neglecting overlap, a modified overlap calculation, 63 and an approximate self consistent field calculation. 69 In all of these calculations we have started with the methyl parameters of Coulson and Crawford. Which are given in Table VIII. The numbering of the atoms is shown in Fig. 12 and the results for the four differente calculations are given in Tables IX-XII. The computer program used to perform these calculations is discussed in Appendix II.

Using the results of these calculations one can calculate the predicted theoretical coupling constants. The hyperconjugation contribution to the methyl and methylene coupling constants, A_H , is given by Eqs. (36 & 37). In addition to this one must consider the contribution of spin exchange polarization, A_p . Following the treatments of McConnell¹⁵ and Colpa⁶⁴ we shall assume that this contribution takes the form

(43)

 $A_{p} = Q_{p} \rho'$

-57-

Table VII. Observed Data for Isoprene

	•				
Al	ï	7.91 ^a	±	.03	gauss
A ₂	Ξ	3.42	±	.03	gauss
A 5	=	3.10	±	.03	gauss
A ₆	=	6.50 ^a	.±	•03	gauss
				2	

^a Assigned on the basis of theoretical calculation.

See Fig. 12 for numbering.

Table	VIII.	Methyl	Group	Parameters

$ H_{H} -0.5 \\ H_{C} -0.1 \\ H_{H-C} 2.00 \\ H_{C-C'} 0.76 \\ H_{C-C'} -0.1 \\ H_{C-C$	•	Par	ameter Cou	ulson & Crawford Value
H _C -0.1 H _{H-C} 2.00 H _{C-C} , 0.76	-		H _H	-0.5
H _{H-C} 2.00 H _{C-C} , 0.76		· .	H _C	-0.1
H _{C-C} , 0.76			H _{H-C}	2.00
	-		H _{C-C} ,	0.76
$H_{ij}/S_{ij} i \neq j \qquad 4.0$			H _{ij} /S _{ij} i≒ j	4.0



MU-35056

Fig. 11

Q.,









MU-35081



Ŷ





9-methyl anthracene

MU-35078





9,10 dimethyl anthracene

MU-35079



		· · · · · · · · · · · · · · · · · · ·						• • • • • • • • • • • • • • • • • • •		
° _i				· ·	i	•		· · · · · · · · · · · · · · · · · · ·		
Radical Anion	1	2	3	4	5	6	7	8	9	10
2,3 dimethyl butadiene	• 59080	36243	00793	•13976						
Isoprene	•59852	36850	00822	.14215	36539	• 59346				
l,3 cyclo- hexadiene	-•35438	• 56933	.00193	22390		•				
Toluene ^a	•00000	50000	. 50000	.00000	.00000	.00000				
Cyclohexa- dienyl ⁰	.52765	02131	52593	.08395	.40052					
o-xylene ^C	.28743	57119	.27646	.02869	11778					
m-xylene ^C	• 55930	27594	28703	.58177	02975	.12226				
p-xylene ^a	50000	0	0	0						
Acenapthene	0.00000	41544	.25434	.25972	41355	0.00000	00875	.15599		
Pyracene	.25154	40421	.00000	00816	.15257					
9 methyl anthracene	43215	.09000	.30679	21779	21608	• 30779	.08787	43440	.00684	.16399
9,10 dimethyl anthracene	21416	.30389	.08694	42717	.00655	1.16128		: .	· .	
See Fig. 12 for numbering a) Antisymmetric orbital; b) Not an anion; c) Symmetric orbital										

Table IX. Huckel Molecular Orbital Coefficients Neglecting Overlap For Radical Anions

61-
ρ _i		· · · ·			i	•		. `	· .	
Radical Amion	1	2	3	4	5	6	, 7	8	9	10
2,3 dimethyl butadiene	.44097	.05582	00614	.00935						
Isoprene	.45253	.06020	00639	.00996	.05365	.43005		· · · · · · · · · · · · · · · · · · ·		
l,3 cyclo- hexadiene	•06382	•39142	01433	.05909		•				
Toluene b c	•38308 ••38378	.03610 .46268	.05824 .45230	•37253 ••37998	01122 00264	.06693 06357		· ·		
Cyclohexa- dienyl ^d	•35912	10667	.36418	03949	.16534					
o-xylene ^C	07091	.68814	09563	00476	01684					
m-xylene ^C	.66512	10156	06874	.71951	00483	01217				
p-xylene b c	.04739 .46114	•35 <u>3</u> 60 -•36083	01074 00214	•06236 ••05932						
Acenapthene	03497	.21409	•04325	.05130	.204.78	03361	00672	.02759		
Pyracene	.04699	.19858	03214	00640	.02691		·			
9 methyl anthracene	.24110	02193	.11243	.03374	.03296	.11293	02163	.23740	00799	.03249
9,10 dimethyl anthracene	.03281	.11021	02073	.23137	00769	.03172				
a) I See I	Ref. 69. λ Fig. 12 for	= 1.00; numberin	b) Antisy	mmetric or	bital; c)	Symmetri	c orbital;	d) Not a	n anion	

62

Table X. McLachlan^a SCF Spin Densities for Radical Anions

Υ.,

э.

· · · · · · · · · · · · · · · · · · ·						·				
C _i		· · · · · · · · · · · · · · · · · · ·			i			· ·		
Radical Anion	1	.2	. 3	.4	5	6	, 7	8	9	10
2,3 dimethyl butadiene	.58241	38633	.06282	.05587						
Isoprene	•56883	36376	.05986	.05324	39355	.61542				
1,3 cyclo- hexadiene	.35163	59989	.07507	.06676						
Toluene ^b	.00000	• 50000	.50000	•00000	.00000	.00000				
Cyclohexa- dienyl ^c	•54579	07020	. 52774	.21499	.19119					
o-xylene ^b	28169	• 56989	30137	.04158	.03698					
m-xylene ^b	.58917	30095	28171	•55150	.03889	.03459				
p-xylene ^b	50000	00000	.00000	.00000						
Acenapthene	.00000	40673	.28365	.20891	42935	.00000	.09450	.08404		
Pyracene	.44298	26220	34023	.05475	.04869					
9 methyl anthracene	.41132	09225	30925	.23096	.20566	32321	06069	.44267	08058	07166
9,10 dimethyl	21782	•32198	.06384	41635	.07455	.06630				
a) R	ef. 63; b) Antisym	metric orbi	tal; c)	Not an ani	on.				

Table XI. Bolton <u>et al</u>.^a Modified Overlap Molecular Orbital Coefficients for Radical Anions

-63-

						_				I
C _i			· · · · · · · · · · · · · · · · · · ·		i		····			
Radical Anion	1	2	3	24	5	6	7	8	9	10
2,3 dimethyl butadiene	.64084	39121	01423	.15240						
Isoprene	.65178	40027	01489	.15604	39465	.64263				
l,3 cyclo- hexadiene	38223	.61114	.02136	24583						
Toluenea	Ö	-•57735	•57735	0	0	0				
Cyclohexa- dienyl ^b	•52769	02089	52603	.08230	.40056					ę
o-xylene ^a	•33094	65647	.31482	.04208	13879					
m-xylene ^C	.63862	31384	33016	.67182	04405	.14545				
p-xylene ^a	•57735	0	0	0						
Acenapthene	.00000	45033	.27405	.28356	44661	.00000	01550	.16788		
Pyracene	27219	·¥3550	.00000	.01433	16373					
9 methyl anthracene	.45672	09480	32346	.22908	.22836	32388	09391	.45766	00286	17345
9,10 dimethyl anthracene	22539	•31915	.09263	45031	00273	.17067				
a) <i>I</i>	Antisymmetr	ric orbita	l; b) Not	an anion;	c) Symm	etric orbi	tal			

Table XII. Huckel Molecular Orbital Coefficients Including Overlap for Radical Anions

-64-

· ·

↓ *1*.

ъ

٤

. Эл

è

: •

where ρ' is the total spin density on the unsaturated carbon to which the methyl or methylene group is attached. Of course in the case of a methylene group one must add the spin densities on the two carbon atoms to which the group is attached to get the total spin density ρ' . As is shown in the next section a good estimate for Q_p in the case of a methylene group would be 2.78 gauss, and we assume that this is also valid for a methyl group. Since, as shown by Colpa,⁶⁴ the hyperconjugation and spin polarization mechanisms act with opposite signs the total theoretical coupling constant A is given by

$$|\mathbf{A}| = ||\mathbf{A}_{\mathrm{H}}| - |\mathbf{A}_{\mathrm{P}}||$$

$$(44)$$

Using this equation we have calculated the series of theoretical coupling constants shown in Table XIII.

The methyl substituted benzenes (toluene and the xylenes) present an additional complication. It is well known that the six-fold symmetry of benzene requires that the first two anti-bonding molecular orbitals be degenerate. In this case the molecular wave function of the unpaired electron can be described only by a linear combination of the two degenerate orbitals. The methyl group in toluene and the xylenes can be looked upon as a perturbation on the six-fold symmetry, and the effect. of this perturbation is to lift the degeneracy of these two levels. The magnitude of the perturbation is such, however, that the two levels are not split very much (e.g. 0.025 β_0 in toluene) and there is still a vibronic mixing of these two near degenerate states. For simplicity we have ignored this additional mixing with the following exceptions. The approximations in these calculations are such that the ináccuracies in energy of the molecular orbitals are far larger than the splitting between

Radical Anion	Expt. ^a	Huckel without , overlap	McLachlan	Bolton overlap	Huckel with , overlap
2,3 dimethyl butadiene	1.200	3.61	1.82	• 59	4.22
Isoprene	(3.42)	3•73	1.94	• 55	4.42
l,3 cyclo- hexadiene	11.114	14.30	17.99	1.09	16.98
Toluene	75 0.79	0.00	(0.57) ^b	0.00	0.00
Cyclohexa- dienyl ^C	64 47•7	53.83	51.26	19.47	53.68
o-xylene	74 2.00	2.36	3.50	.18	3.19 🗧
m-xylene	75 2.26	2.54	2.55	.16	3.51
p-xylene	75 0.10	0.00	(.52) ^b	0.00	0.00
Acenapthene	7.53 64	6.89	8.34	3.01	7.80
Pyracene	64. 6.58	6.60	8.14	•99	7.44
9-methyl anthracene	63 4.27	5.22	6.38	1.13	5•77
9,10 dimethyl anthracene	63 3.88	5.05	6.23	•95	5.58
a) Superscrip b) Computed :	pts give r from ρ = ρ	eference numb Antisymmetric	per. c ^{+ o} symmetri	c	

「日本のない」

Table XIII. Calculated and Experimental Methyl and Methylene Coupling Constants for Radical Anions

-66-

the two near degenerate orbitals. Consequently the calculation is unable to predict which of the two is really lower in energy. We have therefore in each case chosen the one that gives the best fit to the experimental data not only at the methyl groups but at the various ring protons. It turns out that there is never any ambiguity as to which is the "best" The implication of this is that while the simple calculation orbital. cannot predict which orbital is lower there is still not very much mixing, and that one of the orbitals still gives a fair approximation to the true wave function.⁸⁸ The only exception to this is the self consistent field calculation on toluene and paraxylene. These two molecules to a first approximation have nodes through the methyl groups and the inclusion of electron-electron interactions leads to two near degenerate orbitals such that neither of them provide even an approximate description of the unpaired orbital. In this case only, we have calculated the methyl group coupling constant from a wave function Ψ where

$$\Psi = \Psi_1 + \Psi_2$$

(45)

and Ψ_1 and Ψ_2 are the two near degenerate orbitals. These approximations represent a simple approach to a quite complicated subject that has been considered in detail elsewhere.⁹³

The results listed in Table XIII are quite gratifying and indicate that the simple Huckel theory is capable of predicting not only ring coupling constants but also those due to methyl and methylene protons. Of the cases considered with simple Huckel theory none are wildly in error and most provide better agreement with experiment than would be expected from such a simple theory. It is interesting to note that with but one exception the Huckel theory predicts coupling constants slightly larger than those actually observed. This indicates that the calculation

-67-

could be further improved by altering the parameters of Coulson and Crawford to reduce the extent of the hyperconjugation somewhat. This is not terribly surprising since these parameters are quite arbitrary and would be expected to be somewhat in error. The utility of the theory lies in the fact that-it-is-not-very-sensitive to the choice of matrix elements, and that any reasonable selection can be expected to lead to reasonable results. An example of this may be seen in the fact that even with this inaccurate choice of matrix elements the calculation is very successful in predicting the relative magnitudes of coupling constants in several pairs of similar molecules (e.g. ortho and meta xylene, methyl and dimethyl anthracene, methyl- and dimethylbutadiene, pyracene and acenapthene, etc.).

The inclusion of the effect of electron-electron repulsion in the McLachlan calculation does not seem to lead to a significant improvement in agreement. Here again the effects of hyperconjugation seem to be somewhat overemphasized and an adjustment of the parameters so as to scale down this effect would probably be in order. The one case in which the McLachlan calculation does offer a significant improvement over the simple Huckel theory is that of dimethylbutadiene where the McLachlan calculation more nearly predicts the quite small methyl coupling constant.

One obvious conclusion of these calculations is that the theory of Bolton <u>et al</u>.⁶³ does indeed predict coupling constants that are far lower than those actually observed. This behavior was predicted by Colpa and deBoer⁶⁴ and certainly seems to be born out by comparison with a large number of experimental coupling constants. Thus if one wishes to include the effects of overlap the only effective method appears to be the complete overlap calculation including overlap between the unsaturated carbon atoms.

-68-

However the inclusion of overlap in any form appears to add little to the calculation and in fact seems to give a somewhat worse fit than the same calculation performed while neglecting overlap. This has generally been the case for purely aromatic calculations and seems to carry over to the case of hyperconjugation.

Using McConnell's relationship (Eq. (7)) one can also compare the unsaturated proton coupling constants with the predictions of the above calculations if the value of the parameter Q is known. Assuming that Q has the same value as in the case of butadiene (20.82) we have calculated the predicted values for the unsaturated protons of dimethylbutadiene, isoprene, and cyclohexadiene. There are shown in Table XIV. Here again a fair agreement can be obtained with any of the theories used. Since the Huckel, overlap, and modified overlap theories differ primarily in how they treat the effect of the methyl substituent one would expect them to give essentially identical results for the unsaturated protons and this is seen to be the case. The McLachlan self-consistent field calculation in many cases corrects the simple Huckel theory in the proper direction but tends to overcorrect. More satisfactory results could probably be obtained by lowering the value of lambda used in this calculation thus reducing the effects of electron correlation. It should be noted that the Huckel and Bolton theories give different predictions as to which of the methylene groups in isoprene have the larger coupling constant. It would be of some interest to measure the spectrum of the deuterated molecule (if it can be prepared) to determine experimentally which is larger.

The calculations described above can also be performed for the case of the radical cation. Unfortunately we have no new experimental data to

-69-

Molecule	Position ^b	Expt.	Huckel without overlap	McLachlan	Bolton overlap	Huckel with overlag
2,3 dimethyl- butadiene	l .	7.137	7.27	9.18	7.06	7.24
Isoprene	1	7.91	7.46	9.42	6.74	7.49
	5	3.10	2.78	1.29	3.22	2.74
	6	6.50	7.33	8.95	7.89	7.28
Cyclohexa- diéne	l	1.996	2.61	1.33	2.57	2.59
· · · ·	2	8.212	6.75	8.15	7.49	6.61

Table XIV. Calculated and Experimental Unsaturated Coupling Constants for Radical Anions^a

a) Calculated assuming Q = 20.82

b) See Fig. 12 for numbering

offer in a field distinguished by a lack of such data and the results of these calculations are therefore consigned to Appendix III.

C. Justification of the Hyperconjugation Model: Cycloheptatriene

In the last section we showed that methyl and methylene proton coupling constants could be satisfactorily explained by a hyperconjugation model. Several investigators have offered arguments to support the theory that the hyperconjugation model is the only model that can explain these coupling constants. Bolton and co-workers⁶³ postulated that the pairing principle of Huckel theory, ^{76,77} which predicts that the radical cations and anions of a given alternate hydrocarbon should have very similar ESR spectra, would be carried over to methyl coupling constants if these coupling constants arose via a spin polarization mechanism. However if hyperconjugation were the principle mechanism there would be no reason for cation and anion methyl coupling constants to be equal. They took the experimental fact that they are not equal as evidence that the principle mechanism was indeed hyperconjugation. From their calculation they predicted a series of ratios $A^+_{methyl}/A^-_{methyl}$ which were in good agreement with the experimental ratios. However, as we have seen, the absolute magnitude of their coupling constants is seriously in error and this throws some doubt on their whole theory.

Colpa and deBoer⁶⁴ used a corrected hyperconjugation theory and were able to successfully predict both the anion/cation ratios and the absolute magnitude of the coupling constants in a number of cases. In addition, they performed a configuration interaction calculation on the C'-CH₂ fragment (C' being the unsaturated carbon to which the methylene group is attached) to obtain an estimate of the magnitude of the spin exchange polarization mechanism. They found that the spin polarization contribution to methylene coupling constants could be given by

$$A = Q_{SP} \rho_C, = -1.1 \rho_C, \qquad (46)$$

and that this Q.value was far too small to account for the large coupling constants observed. They point out that the approximations in such a calculation naturally leave the numerical results in some doubt. Nonetheless they felt that the order of magnitude of the results substantiated their main argument.

The ESR spectrum of the cycloheptatriene radical anion offers a striking experimental confirmation of the importance of hyperconjugation. Moreoever from the hyperfine coupling constants it is possible to obtain a quantitative measure of the magnitude of $Q_{\rm SP}$. This is brought about

by the fact that symmetry considerations require the first anti-bonding molecular orbital of cycloheptatriene to have a node passing down the symmetry axis which goes through the methylene carbon. This means that for reasons of symmetry there can be no hyperconjugation contribution to the methylene coupling constant, and consequently any resulting coupling constant can only be the result of spin polarization or electron correlation.

We have prepared the cycloheptatriene radical anion by electrolyzing a three millimolar solution of the parent hydrocarbon dissolved in a solution of liquid ammonia. The solution was saturated with tetramethylammonium iodide. No electron appeared at electrolysis voltages up to 100 volts but at the higher voltages a bubbling occurred at the cathode presumably due to some decomposition reaction. The spectrum obtained is shown in Fig. 13.

The spectrum is moderately complicated but the assignment is made considerably easier by the fact that the two outermost triplets are so well resolved. As in the case of cyclohexadiene a reasonable guess would be that one coupling constant is given by the distance between the two triplets and one coupling constant is given by the spacing within either triplet. Sincere there are only four coupling constants in the problem these guesses plue the total width constraint leaves but one coupling constant undetermined. This last coupling constant may then be determined by trial and error with very little difficulty. The resulting assignment is given in Table XV, and the theoretical spectrum calculated from this assignment is shown in Fig. 14. As can be seen there is excellent agreement between the theoretical and experimental spectrum.

With no further experiments it is impossible to assign which of the coupling constants in Table XV are associated with which protons.

1

-72-



MU-35082

Fig. 13



Fig. 14

Table XV. Observed Coupling Constants for Cycloheptatriene

$A_2 = 2.16 \pm 0.03$	gauss
$A_3 = 7.64^a \pm 0.02$	gauss
$A_{4} = 0.59^{a} \pm 0.03$	gauss
$A_{5} = 4.90^{a} \pm 0.01$	gauss

* Assigned on the basis of theoretical calculation

See Fig. 15 for numbering

be seen from Fig. 15 the molecule contains four sets of two symmetrically equivalent protons each. In order to determine which coupling constant was associated with the methylene protons we prepared the radical anion of cycloheptatriene in which one of the methylene protons had been replaced by a deuterium. The ESR spectrum of this deuterated species is shown in Fig. 16. The coupling constant of a deuteron is given by

$$A_{\rm D} = \frac{\mu_{\rm D}}{\mu_{\rm H}} \frac{I_{\rm H}}{I_{\rm D}} A_{\rm H} = 0.1535 A_{\rm H}$$
(47)

where the μ 's are the magnetic moments as they are commonly tabulated, the I's are the spins of the deuteron and proton, and A_H is the coupling constant for a proton occupying the same position in the molecule. From this it is possible to calculate the four possible spectra expected from the deuterated species. These are shown in Fig. 17. A comparison of



-MU-35083

Fig. 15

,

•



Fig. 16



Fig. 17

Figs. 16 and 17 clearly shows that the methylene proton coupling constant is 2.16 gauss. The other coupling constants cannot be assigned directly from the experimental spectra but can be assigned with considerable confidence from the following theoretical considerations.

We have performed the same series of calculations that was described in the last section on cycloheptatriene. The numbering system used is shown in Fig. 15 and the results of these calculations are given in Table XVI. Of course, since there is a node at the methylene group the results of the three non-correlation calculations will be the same since they differ only in their treatment of hyperconjugation. These calculations indicate that there is a large spin density on the two carbon atoms to which the methylene is attached, and the largest experimental coupling constant tends to confirm this fact. If spin polarization were the principle mechanism for producing unpaired spin density on the methylene groups of all radicals we would expect a very large methylene coupling constant in the cycloheptatriene radical anion similar to that which one finds in cyclohexadienyl, cyclohexadiene, and similar radicals. The fact that the methylene coupling constant is only 2.16 gauss confirms the fact that hyperconjugation, which in this case is absent, is generally the principle mechanism for methylene coupling constants.

The fact that hyperconjugation is not effective in this radical allows us to obtain an experimental value for the constant $Q_{\rm SP}$. The McLachlan calculation predicts that essentially all the spin density is in the unsaturated part of the molecule and that the spin density at position 4 is négative. Assuming that this is correct we can obtain a value for Q given by

-78-

Position ^a		Huckel Coefficient	McLachlan Spin Density ^b
1		0	-0.00095
2		0	-0.00338
3		-0.52112	0.35819
4	• · · ·	0.23192	-0.02280
5		0.41791	0.16677

Table XVI. Molecular Orbital Coefficients and Calculated Spin Densities in Cycloheptatriene Radical Anion

- a) See Fig. 15 for numbering
- b) Reference 69. $\lambda = 1.00$

$$Q = 2\sum_{i=3}^{5} A_i = 23.90$$
 (48)

Using this Q, the experimental coupling constant A_3 , and Eq. (7) one finds that the unpaired spin density on carbon 3 is 0.320 and the total unpaired spin density adjacent to the methylene group is 0.639. The total methylene coupling constant consists of a small hyperconjugation part and a larger spin polarization part. Using the spin densities predicted by the McLachlan calculation and Eq. (36) we can estimate the electron correlation induced hyperconjugation contribution to be 0.38 gauss. As has been mentioned the spin polarization and hyperconjugation coupling constants are ordinarily of opposite sign, but in this case the hyperconjugation is caused by a negative spin density, the two effects add, and the spin polarization coupling constant is

 $|A_{SP}| = |A_{total} - A_{hyperconjugation}| = 1.78$ gauss (49)

This coupling constant and the adjacent spin density determined above may be inserted into Eq. (46) to give the value $Q_{\rm SP} = 22.78$ gauss. This is remarkably close to Colpa and deBoer's calculated value of -1.1 when one considers the approximate nature of their calculation. It has been suggested 7^{8-80} that aliphatic coupling constants are a function of the angle θ between the normal to the pi system nodal plane and the C'-C-H plane, and that the relationship is given by

$$A = B_0 + B_1 \cos^2 \theta \qquad (50)$$

The parameter B_{O} in this formula is the same as our Q_{SP} and to the best of the author's knowledge this is the first experimental determination of this quantity.

Using the Q value given in Eq. (48), the theoretical spin densities, and McConnell's relationship one can calculate a set of theoretical coupling constants for the unsaturated part of the cyclopheptatriene radical anion. This has been done and the results are shown in Table XVII. As can be seen there is a reasonable agreement between theory and experiexperiment. The self-consistent field theory is particularly useful to explain the quite low coupling constant of carbon number 4, although again one gets the feeling that perhaps the value of λ should be reduced to reduce the electron correlation effect.

An obvious experiment that suggests itself is to measure the ESR spectrum of the 1,3,5-hexatriene radical anion. Here again one could take advantage of the fact that the hyperconjugation in cycloheptatriene is symmetry forbidden. Thus the only difference between the pi-electron

-80-

Position ^b	Expt.	Huckel	McLachlan	,
	7.•64	6.49	8.56	~
4	0.59	1.29	0.54	
5	4.90	4.17	3.99	

Table XVII. Calculated and Observed Unsaturated Coupling Constants for Cycloheptatriene Radical Anion^a

a) Calculated assuming Q = 23.90

b) See Fig. 15 for numbering

distribution in hexatriene and cycloheptatriene would be the inductive effect of the methylene group. In most methyl or methylene groups the electron distribution is perturbed by combined hyperconjugation and inductive effects and the separating of these two effects is a matter of considerable theoretical interest. In this pair of molecules the hyperconjugation effect is nonexistent and a comparison of the unsaturated proton coupling constants in the two molecules should provide an experimental measurement of the inductive effect alone.

Unfortunately our efforts in this direction have been only partially successful. We have attempted to prepare the radical anion of hexatriene by electrolysing solutions of hexatriene dissolved in various concentrations in liquid ammonia. Various supporting electrolytes were used in an attempt to increase the lifetime of the radical. In this series of experiments only one succeeded in producing even a weak spectrum and even this one was not reproducible. A very rough measurement indicated that

Ľ.

the two largest coupling constants were 7.3 and 4.2 gauss. The lack of resolution and sensitivity made the measurement of the third coupling constant very difficult but the lack of readily observable splittings probably places an upper limit of 0.5 gauss on it. There are some very poorly resolved lines that could be the result of a coupling constant of around 0.5 gauss.

No really quantitative conclusions can be drawn from these very poor data. The fact that the hexatriene coupling constants seem to be so close to the cycloheptatriene coupling constants indicates that the inductive effect of the methylene group is small. This is not unreasonable in view of the fact that the model used in the previous section completely neglected any inductive effects and was still relatively successful in predicting unsaturated coupling constants. The fact that both large coupling constants in hexatriene are smaller than the corresponding cycloheptatriene coupling constants is interesting. The change is probably large enough to be real and not just an experimental error and it could be caused by one of two effects. First of all the sigma-pi interaction could have changed in such a manner as to lower the Q value. If this were the case and if the third coupling constant were still 0.6 and caused by negative spin density the Q for hexatriene would have to be around 21.8. Changes in Q of this order are certainly not impossible but it seems to be a rather large shift for two such similar molecules. The more likely explanation would be that the effect of eliminating the methylene group was to rearrange the pi-electron density such that the spin density at position 4 (position 2 in hexatriene) was no longer negative. A positive spin density coupling constants of 0.4 gauss at position 2 would be sufficient to account for the shifts in the larger coupling constants without any change in the value

「たい」

N. 1. 1911 .

-82-

of Q. The comparison of Huckel, McLachlan, and experimental coupling constants in Table XVII. indicates that electron correlation has a considerable effect in cycloheptatriene, and it would not be surprising that this correlation effect would be sensitive to the removal of the methylene group. Obviously better data are needed for more quantitative arguments and further work along this line is in progress.

D. Nitrosobenzene and Nitrobenzene

We have prepared the radical anions of nitrosobenzene (C_6H_5NO) and nitrobenzene ($C_6H_5NO_2$) by electrolysis in liquid ammonia solution. The nitrosobenzene radical anion shows two ortho and two meta proton coupling constants which can be explained by simple theoretical models. The nitrobenzene radical anion was prepared in liquid ammonia as a reference and to compare solvent shifts.⁸¹

The observed spectrum of the reddish-brown nitrosobenzene radical anion is shown in Fig. 18. This radical appears to be quite stable at -78° C. in liquid ammonia solution. It is far more stable than any of the other radicals so far discussed and is probably more stable than even nitrobenzene. The spectrum consists of 30 principal lines which are further split by small amounts. On the basis of the 30 principal lines one can readily determine the N¹⁴, the single para proton, and average values for both the ortho and meta coupling constants. The larger value can be assigned to the ortho protons in analogy to nitrobenzene. The additional splittings can only be accounted for if it is assumed that nitrosobenzene has two ortho protons differing by 0.30 gauss. A similar difference for the meta protons of 0.18 gauss can be determined from the intensity ratios within its triplets. The calculated spectrum in Fig. 19

-83-



MU-35084

Fig. 18



MU-35085

Fig. 19

-- shows the excellent agreement with experiment for the coupling constants given in Table XVIII.

The two ortho and two meta coupling constants must arise from the effects of a non-linear C-N-O group. This group must be held fairly rigidly in a planar conformation or else the difference in coupling constants would be averaged out by rapid internal rotation. This is similar to the case of nitrobenzene, but the symmetry of nitrobenzene does not allow us to determine directly the effects of the N-O bond on the coupling of the ring protons.

A theoretical interpretation of this effect can be included in a Huckel LCAO molecular orbital calculation of the spin densities in either of two ways. One can either utilize a small resonance integral between the oxygen and the nearby ortho carbon (between positions 1 and 8) or describe the polarization effects of the nitroso group by changing the Coulomb integral of one ortho carbon atom. Rieger and Fraenkel⁹⁴ used the latter method and Stone and Maki⁸⁴ used both methods to account for similar asymmetries in substituted benzaldehydes. Stone and Maki referred to these as the β - and α -effects respectively. If one uses the approximate configuration treatment of McLachlan with the parameters recommended by Reiger and Fraenkel⁸¹ but with $\delta N = \frac{1}{3} \delta N \stackrel{60}{} \delta N$ and with $\gamma_{18} = 0.05$ or $\delta_8 = -0.07$ then one obtains the theoretical proton coupling constants given for nitrosobenzene in Table XVIII.

It can be seen from Table XVIII that either a small value for the resonance integral between the oxygen and its nearby ortho carbon or a small change in the nearby ortho carbon Coulomb integral yields a satisfactory explanation of the two ortho and meta coupling constants. As previously observed⁸⁴ these two effects are seen to work in opposite directions and we are unable to distinguish between them. An arbitrary

-85-

Position	Obs. ^b	βeffect ^d	Cal. ^C	α effect ^e
Nitrogen-2	7•97±•01	-		-
Para H-6	2.97±.02	4.43		4.54
· Ortho H-4	(3.84±.02	3.68		4.02
-8	(4.14±.02	4.03		3.67
Meta H-5	(0.96±.02	1.08		1.22
-7	(1.14±.02	1.22		1.06

Table XVIII. Coupling Constants for Nitrosobenzene and Nitrobenzene Radical Anions^a

' Absolute magnitudes in gauss

Bracketed values may be interchanged

Calculated with $\delta_0 = 1.4$, $\delta_N = 0.733$, $\gamma_{NO} = 1.67$, $\gamma_{CN} = 1.2$, and

 $Q_{CH}^{H} = 23.7.$ The meta positions have negative spin density.

¹ Using $\gamma_{CO} = 0.05$ between positions 1 and 8. $\rho_1 = 0.2629$, $\rho_2 = 0.3138$, $\rho_3 = 0.0086$.

^e Using $\delta_8 = -0.07$. $\rho_1 = 0.2652$, $\rho_2 = 0.3121$, $\rho_3 = 0.0026$.

adjustment of parameters can improve the agreement with the values in Table XVIII particularly for the para position. This effect may be seen in Table XIX where we have listed the results obtained by performing the McLachlan calculation with various values of δ_{N}^{*} .

Value of δ_{N}	4	5	Position 6	7	8	
0.80	3.59	1.07	4.26	1.23	3•99	
1.00	3.41	1.08	3.81	1.22	3.77	
1.20	3.20	1.07	3.36	1.20	3.53	
1.40	2.97	1.07	2.92	1.18	3.28	
1.60	2.74	1.07	2.49	1.16	3.02	
1.80	2.51	1.07	2.06	1.15	2.76	
2.00	2.29	1.08	1.64	1.15	2.51	
2.20	2.10	1.10	1.24	1.15	2.28	
Expt.	3.84	0.96	2.97	1.14	4.14	

Table XIX. Calculated^b Proton Coupling Constants for Nitrosobenzene Radical Anion^a

^a Absolute magnitudes in gauss.

^b Calculated with $\delta_0 = 1.4$, $\gamma_{\rm NO} = 1.67$, $V_{\rm CN} = 1.2$, Q = 23.7, and $\gamma_{18} = 0.06$.

In Table XX we give our observed values for the radical anion of nitrobenzene in liquid ammonia. The radical anion was prepared by the electrolytic reduction of a 5×10^{-3} M solution 0.1 M in sodium iodide. The spectrum was independent of temperature from -40 to -78°C. Also given are values for nitrobenzene dissolved in dimethylformamide, ⁸¹ acetonitrile, ³³ and 50% water in acetonitrile, ⁸² respectively. It can be seen from Table XX that the solvent shift for nitrobenzene in liquid ammonia is intermediate between acetonitrile and 50% water in acetonitrile.

Ludwig <u>et al</u>.⁸² have recently related the large solvent shifts for nitrobenzene radical anion to the formation of hydrogen bonds with the solvent. Since acetonitrile and liquid ammonia have essentially the same value for their dielectric constants the shift cannot be explained entirely by the simple polarity of the solvent. Since liquid ammonia is a more protic solvent than is acetonitrile, its position in the solvent shifts in Table XX is consistent with some type of hydrogen bonding. However, it can also be seen from Table XX that the calculation of Reiger and Fraenkel⁸¹ which is based upon a variable oxygen coulomb integral is a very satisfactory qualitative interpretation of the shift in the nitrogen and proton coupling constants in a wide variety of solvents.

E. Cyclooctatetraene

By far the most dramatic solvent effect which we have observed in liquid ammonia is in the radical anion of cyclooctatetraene. This radical has been prepared by Katz and Strauss⁸³ by alkali metal reduction in tetrahydrofuran. They observed a spectrum due to eight equivalent protons with a coupling constant of 3.209±0.007 gauss. From the intensity of the radical spectrum they concluded that the equilibrium for the disproportionation reaction

-88-

	Position	Ammonia	Dimethyl- formamide ^a	Acetonitrile ^b	50% H ₂ 0 in CH ₃ CN ^C
	N	11.46	9•70	10.32	13.59
	Para	3.89	4.03	3.97	3•5 ⁴
	Ortho	3.42	3•36	3•39	3.44
	Meta	1.11	1.07	1.09	1.12
a b c	Ref. 81 Ref. 33 Ref. 82				

Table XX. Nitrobenzene Radical Anion Coupling Constant Solvent Shifts

$$2R^{-} = R + R^{2-}$$

was shifted far to the right.

We have prepared the radical anion of cyclooctatetraene by electrolysis of a dilute solution of the hydrocarbon in liquid ammonia. The solution was saturated with tetramethylammonium iodide. The spectrum was found to be that of eight equivalent protons with coupling constant 3.278±0.004 gauss. The one striking feature of the spectrum was its high intensity and extreme stability. ^{*} Although no quantitative measurements

The radical spectrum was so strong that trace amounts of hydrocarbon remaining in the vacuum system contaminated the system, and nothing but cyclootatetraene spectra could be produced for several days after the initial experiment.

(51)

were made it seems safe to conclude that the effect of switching solvents from tetrahydrofuran to ammonia was to shift equilibrium 51 drastically to the left. The effect was so pronounced that it is doubtful that this can be looked upon as a solvent perturbation. It seems more likely that the entire chemistry including ion dissociation and perhaps even geometry of the molecular species changes when ammonia is used. Further work on the chemistry of this system is now in progress.⁸⁹

-90-

One additional interesting feature of this system is the change in coupling constant of 0.069 gauss. Although far larger coupling constant solvent shifts have been previously observed, ⁸¹ symmetry considerations in this molecule require a different mechanism than is usually thought to be responsible. Ordinary solvent shifts are usually regarded as arising from a redistribution of the unpaired pi-electron spin density caused by solvent perturbations. Since coupling constants are related to unpaired spin density distribution by Eq. (7) this would bring about a coupling constant shift. In this molecule however symmetry considerations require that one-eighth of the odd electron reside on each carbon atom. Thus the quantity effected by the solvent perturbation is the sigma-pi interaction parameter Q. This Q-shift is small ($\Delta Q = 0.55$ gauss) as would be expected but is certainly larger than experimental error. A variation of the Q of the benzene radical anion with temperature has been observed by Fessenden and Ogawa.⁹⁰ The variation in this case is about the same order of magnitude as we have observed in cyclooctatetraene and is in the direction of producing lower Q values at lower temperatures. Although a detailed theoretical consideration of these effects is complex and quite outside the scope of this work, we note that a mechanism involving ion pairing would be consistent with the direction of the shift in both of these cases.

ACKNOWLEDGMENTS

I am indebted to Professor Rollie J. Myers for his constant encouragement and expert advice throughout the course of this work.

The exchange of ideas with my colleagues and their frequent assistance has been an invaluable aid which I gratefully acknowledge.

Mrs. Pat Cookson has been particularly helpful in coping with the bureaucracy when it threatened to overwhelm us. I am further indebted to her for typing this thesis.

I wish to thank my wife for proofreading, editing, tea and sympathy. This work was completed under the auspices of the United States Atomic Energy Commission and the Lawrence Radiation Laboratory.

APPENDIX I

Fortran II Computer Program ESR IV

-92-

The theoretical calculations and drawings in chapter four were done with the aid of the computer program ESR IV. This program uses the same basic method of calculation as the program ESR III developed by Stone and Maki⁸⁴ with the exception that ESR III will handle directly only 4 equivalent I = $\frac{1}{2}$ and 3 equivalent I = 1 nuclei while ESR IV will handle any number of equivalent nuclei.^{*} The principal difference is in the output.

ESR IV has deleted the three types of output available in ESR III and uses a California Computer Co. digital x-y plotter as an output device. The program makes use of the binary subroutine package J6 XYP2 MOD⁸⁵ which is usable only on an IBM 7094 computer. The 7094 produces a tape which is used as input to an IBM 1401 (or 1460) computer which drives the plotter. The 1401 is under control of the IBM 1401 PARASITE PLOT Program and any future changes in this program will probably require changes in ESR IV.

There are two basic outputs available with ESR IV. The first produces a plot of the spectrum with the name of the problem lettered above it for identification and nothing else. All input information is written on the 7094 monitor print tape for ordinary 1403 printing. The second output in addition provides a one-inch grid with the horizontal axis labeled in gauss and prints the input data on the graph itself to the right of the spectrum if the spectrum involves only one species. If more than one species is involved, the program leaves room for printed data to be stapled next to the spectrum and prints the input data on the 1403.

The author would like to thank Drs. Stone and Maki for a listing and deck of their program.

The second output is rather elegant but uses a great deal of plotter time (up to 15 minutes per graph) to draw the grid and print the input data. The first output is not quite as pleasing but probably uses a maximum of 30 seconds of plotter time. In regard to 7094 time, ESR IV is somewhat faster than ESR III regardless of which output is used.

The data cards are divided into group A, which applies to the entire problem, and group B, which applies to one species. There must be a set of group B for each species to be superimposed, and they are stacked in any order after group A. Definitions of all input variables are given after the following list of data cards. Each card must be included unless otherwise indicated.

FORMAT	CONTENTS	COMMENTS
•	Group A	
(12A6)	ANAME(I), $I = 1,12$	
(214)	NSPEX, KSHAPE	
(2F12.6, I12)	GPI, HIY, LETTER	
	Group B	
(12A6)	BNAME(I), I = 1,12	
(214)	NA, NB	
(3F12.6)	WEIGHT, WLINE, PHASE	
(6(I4, F8.3))	NQA(I), A(I), I = 1, NA	May be omitted if $NA = O$
(6(I4, F8.3))	NQB(I), A(I), I = 1, NB	May be omitted if $NB = O$

As many calculations may be stacked on top of each other as desired. At the end of the entire data deck there must be two blank cards.

-93-

Definitions of Input Variables

ANAME	The name of the problem. This will be lettered across
	the top of the graph.
NSPEX	The total number of species whose spectra are to be
	superimposed.
KSHAPE	If zero, Lorentzian lineshape selected; Gaussian

lineshape for non-zero.

GPI Horizontal scale of spectrum in gauss per inch.HIY Height of largest peak of experimental spectrum in inches. Must be less than ten.

LETTER If zero, output consists of spectrum and title only. If non-zero, grid and input data plotted.

BNAME The name of each species. Will be printed or typed above the input data for that species.

The total number of different coupling constants with $I = \frac{1}{2}$.

The total number of different coupling constants with I = 1.

The relative abundance of the species. If there is only one species any positive number may be used. The linewidth in gauss.

PHASE If +1.0 lines will look like this: If -1.0 lines will look like this: NQA(I) The number of equivalent I = $\frac{1}{2}$ nuclei having the Ith coupling constant.

A(I) The Ith coupling constant for nuclei with $I = \frac{1}{2}$, in gauss. NQB(I) B(I) } The corresponding variables for nuclei with I = 1.

NA

 \mathbb{NB}

WEIGHT

WLINE

Example: The use of ESR IV is illustrated by the following example. The experimental spectrum appears to consist of 2 species with the same g-factor. Species A, in 20% abundance has hyperfine structure from 5 equivalent nitrogens with A = 2.35 gauss. The linewidth is 0.135 gauss. Species B, in 80% abundance, has hyperfine structure from 2 equivalent protons, with A = 3.59 gauss. The linewidth is 0.180 gauss. The highest line measures 4.25 inches peak-to-peak, and the total width of the spectrum is 14.72 inches. Full output is desired, and the lines look like this: $-\sqrt{-}$ The data cards will appear exactly as shown below, where - represents a

blank space.

-FICTITIOUS-EXAMPLE

4 F L - 1

---2---0

-----4.252-----1

-SPECIES-A

---0---1

------2.000-----0.135-----+1.0

---5---2.350

-SPECIES-B

---1---0

---2---3.590

Blank }

Blank

, (if this is the only spectrum being run)

It will be noted that with clever handling of the input data one can produce the full spectrum, deal with nuclear spins greater than 1, deal

-95- .
with two or more species of different g value, and do various other things not explicitly written into the program.

The listing of the Fortran program is as follows:

	\$	40	02	C7		ËΡ	R		•	3	Û	CN	LEV	Y														
	#			LA	BEL								:															
	C٤	PR	Iν	SI	PEC	. FR	UM	\$1	MUL	ATOR	PH	OGR	٨M															
	C	ST	ΑΤ	EM	ENT	. N	IUME	BER	sυ	SED	IN	гне	FC	LOW	[NG	PR	OCR	ΑM	AR	E I	-1	80,	2	30-	23.	2, ·	551,	
	Ċ	61	0-	61	5.	71	1.	10	01-	1005	. 1	101	- 1	106.	. 11	11	-11	.12	. 1	201	-1	207	, .	130	1-	130	2.	
	č	13	ō4	-1	307	•	14(-10	141	9.1	751	. 1	801	-180)6.	26	01-	.26	10.	28	300	, 2	80.	2.	30	01-	3010	
	ř	31	оı	- 3	105	i.	310	57.	50	<u> </u>	500	6.	200	1-60	hos.	. 7	001	- 7	010		100	1-8		3	90	03-	9018	Ŷ
•	C	1	~	nī		1.7	ON	.A M	AME	(13)		(A / 2	600	001	2021	6 A M	E / 1			0 1	500	1.	11	501		0.5	1010	
			·,	MO	216	51	r	215		SCA	ຸ່.	21.	,00 HC	1013	221			: 5 7 : 6 7	121	94/14 1	20	<i>,</i> ,	~	,	,			
•			•	201	501	11-" N	ŕv	61	212	201	221	0.1	10	1.27	710	, A.	11.	2.2	10.	1.1	6)							
			,	20	1 7. 1	//_ () 2	211	· · ·	212	2019		601	120	196.1		1. 1	101	4	5 U J	1 7		200	ir: A			•		
		•	1	77	(~1) / 0	10	2	193	70	,		100	20	1,00	+ (U g) (E)	7 4 7	201	,0	. 7 1 14 	1 1 1	11	300	51	' o 7	1.	~	51	
				00	(0) ()	, L U	201	1.1	110	1091	1000	17	9 6 7 13 E	1 00	, , , , , , , , , , , , , , , , , , ,	,,0	2 (J 5)	• • •	* 27 7 1	9 Q 4 7	г х д . х	,0,	11		11	, 0,	218	
			,	.07	1 1 p 7 (C	109	יני. יו	971	121	1 1 1	101	200	090 011	1201	5 N K 2 1 / 1 / 7) U #	ノ <i>1</i> 9 ヽ ヽ	50	1.4.4	С р . Г . 4		1 20		, , ,	51	*		
			1	12	210	د ور م	9 L I	1 7 1	221	1 / 1	51	126	11	0 51		19-0	1 1 1	20	109	(.g.) (.) (,,,	127	1 A 1	5 U y 1 / 2	1	' ^	5 1	
				1.0		.,0	5	1 2 1	271	1 0	517	1/0	1.7	0,51	1 7 1 3	101	1 0	5 5)) 1	621	1	0,5		140	11		<i>,</i> ,,	
			1	17			. C C	191	411 016	しょしょ	1017	149	1 1 9	10101	1 9 1 -) L L	190	د و ر) , L	221	. 1.9	0,0		100	1.54	000	,	
			ŗ	211	413			141	912	600 C J 6 N	11		+ + +	101					200		0		2					
			۰,	r Ki		01_0 		20		217	200	411	0,1	9211	170		,	7	300	411		1 1 0	2.					
			1	210		N. #	12) 7	11,	210	20	2 4	: 1	1 + 2	2010		* 1	. 29	11	1 2	10	410	91	291	19			
			1	211	221	0,	12:	9 L J 1 L	, 9		. 4 g 1	2)	, 9	01/0			1.	901		TOI	8	210	211	10 1	* 1	1 *		
			1	000		. U 9		119	00		1010	700	, 0	0141			())	0	221	(2)		100		10 1	7 L (7	
•			1	00		10	291	[/y	.00	1911	.19	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	110	9 L 9 I	.001	· • · ·	000	21	201	, 1	. 60	112	001	// ,				
			, ,	1	+00			L 9.	119	140	1110	1	y 1	111	400	10	y 1	. 9	110	14	101	10,		· 1	1.			
			<u>ا</u> ر ا	1	+02			L 9 1	1 J 9 1 J 9	1.10	010	, L	9 I) * 1	.464	10	* T	7	1] 4	14	10.2	10,	11	L L	12			
				1	+ U 7 1 N/ 7		,		1)			•																
			,	PR	LIN D NACA	۰ ۲	1					., -		0.0	0.0													
		τ.	1	r Gr	< M A	. i - 1 - 1	14.	- 110	MUUI	NI B	LAN	KI	APE	UN	85)		•									
				CAL	- L-	PA	05:	-																				
			1	CAL		C A	LSE	: 1	(15)																		
	~		4	FLIP	(MA		(3)	-12	•0)																			•
	в		د.	ANA	AME	1) = c	506	000	CTGZ	30					2.										•		
			4	1-11-1	2 M A		121	101		~ .					~ .												•	•
			2	KL/	10	IN	PUI	E E.	APE	2,4	, (A	NAM	C []	1,1=	2.1	.3)		·	• •									
			{	K 2 4	10	IN	PUI		APE	2,0	, N	SPE	Χş	K2H4	PE		-											
		11	1.	11	(1)	255	EX	2	31,	231	, 9																	
		• •	9	Kr:4	10	1.54	PUi	i).	APE	2.	12,	69	1,	ніў,	- L -		ER	.*										
	د	10.	2	11-		SP	5 X		117 . 	1401	, L	401	, 6															
	. 4	40.	1	15		51	IE R	(). 	10,	6,	10																	
•	~		5	WK I	11.12	្ប	011	101	1 AI	PE 3	2	800												·				
:	2	800	0	FUR	(MA	1		112	INPI	01 U 57 5	AIA)		•													
	-	0.00	<u>,</u>	WR I C O D		្ប	018	101	1 A	rte o	* Ľ	80Z																
	2	804	2	FUR	(M A	· _	127	5 1 1 1 1 1	· T A 4	.					T - 13													
			~	WK 1	: 1 <u>L</u>	τU	011	101	IAI	7E 3	94 9	IAN	NME	(1),	1=2		3)											
	0	, ,	5	TUP	(MA	1	(21	.4)	~ ~ ~	(A A -		c.								÷	- 1	•						
	0		2	000		11	1 -	. 00	1000	5007	023	U								•						•		
		14	2		CMA NGC		(Zr	12.	• • •	112	,	•			,				•									
		11)	NUSP	20	=0 ⊻-	0																					
÷ ,		1 6	7. 5	NDA NC	1.6	~~		4.03	<u>ης.</u>														• •					
		11	ر د	00 V34	. J T Q	1 7 1	-1,	000	00	د																		
		- 40	5 7	1 A L N C O	. 	4 J NI	-U- 00-	· · · ·	1											۰.			•.					
		10	2	1 N 3 P D E A	ົວ	+ N 1 M	556	. U Y J		· ·	10			۱ Y-	,	53												
	·,	103		~ C // 1 C	1.0	1 N 6 D	г U I с Y	_ • •	475 1 1 - 1	ム94 11.000	1 1 1	NAM 202	C (1 1 /	/ / /=	4 % L	51												
	د ۱	401	י כ	151	10	5P TT	50 V	,		(45.Z ≓0	* 1	402	۰ ۲.	·														
		102	5	11" L 110 T	TC	1	657 1170	יבע דווי	ניני. אר	179. DE 5	20	10		= 1 + 1 >	. r	?	. 1 - 2	•				-						
			ś	ne y Be	10	1 11	017 0117	· • • ,	1 A / 1 U C	2 0	9 7 9 . NIA	- NID	VALI	/	* . A	- 2 \$		1										
		21	<i>.</i>	in ga		4 IN	-01	14	4F 6.	£ \$ O	# 18A	110																

```
21 READ INPUT TAPE 2,2, WEIGHT, WLINE, PHASE
  22 IF (NA) 27,27,23
  23 READ INPUT TAPE 2,24, (NCA(1), A(1), 1=1, NA)
  24 FORMAF(6(14,F8.3))
3104 IF (NSPEX - 1) 1403, 1403, 25
1403 IF (LETTER) 2601, 25, 2601
  25 WRITE OUTPUT TAPE 3,26, (NGA(I), A(I), I=1, NA)
  26 FORMAT (10X,13,27H EQUIVALENT, 1=0.5, WITH A= ,F12.6,6H GAUSS )
     STATEMENTS NUMBERED TWENTY-SIX HUNDRED TAKE CARE OF THE
     POSSIBLITY OF MORE THAN 4, I=0.5, EQUIVALENT COUPLING CONSTANTS
2601 NTA=NA
2602 DO 2610 L=1, NTA
2603 NTEMP = NQA(L) -4
2604 IF (NTEMP) 2610, 2610, 2605
2605 \text{ NQA(L)} = \text{NQA(L)} - 4
2606 \text{ NA} = \text{NA} + 1
2607 \text{ NGA(NA)} = 4
2608 A(NA) = A(L)
2609 GD TD 2603
2610 CONTINUE
  27 IF (NB) 3101, 3101, 28
  28 READ INPUT TAPE 2,24, (NCB(I), B(I), I=1,NB)
3105 IF (NSPEX - 1) 1404, 1404, 29
1404 IF (LETTER) 3001, 29, 3001
29 WRITE OUTPUT TAPE 3,30,(NGB(I),B(I),I=1,NB)
  30 FORMAT (10X, I3, 27); EQUIVALENT, I=1.0, WITH A= , F12.6, 6H GAUSS )
      STATEMENTS NUMBERED THREE THOUSAND TAKE CARE OF THE POSSIBILITY
     OF MORE THAN 3 EQUIVALENT, I=1, COUPLING CONSTANTS
3001 NTB = NB
3002 DC 3010 L=1, NTB
3003 \text{ NTEMP} = \text{NQB}(L) - 3
3004 IF(NTEMP) 3010,3010,3005
3005 \text{ NGB(L)} = \text{NQP(L)} - 3
3006 NB = NB + 1
3007 NG8(NB) = 3
3008 B(NB) = B(L)
3009 GC TO 3003
3010 CONTINUE
3101 IF (NSPEX - 1) 1405, 1405, 31
1405 IF (LETTER) 33, 31, 33
  31 WRITE OUTPUT TAPE 3,32,WEIGHT,WLINE
  32 FORMAT(10X,15HSPECIES WEIGHT= F12.6,15H AND LINEWIDTH= F12.6,
    16H GAUSS )
  33 00 35 1=1,2
  34 DO 35 J=1,6000
  35.YA(I,J )=0.0
  36 W10=0.0
  37 TENS=1.0
  38 IF (NA) 43,43,39
  39 DC 42 I=1,NA
  40 ANQ=NQA(1)
  41 WID=WID+(ANQ*A(I))
```

- 41 wid-wid-(ARGCATIT) 42 TENS=TENS*(2.0**ARG)
- 43 IF (NE) 48,48,44
- 44 DC 47 1=1.NB
- 45 BNQ=NQB(I)

С

C.

C.

46 WID=WID+(2.0*8NQ*8(I)) 47 TENS=[ENS+(3.0**8NQ) 48 HAF=WID/2.0 49 NI=WLINE/0.005 50 NGEN=16+NI 51 NORG=8*NE 52 ORIGIN=0.005*FLCA(F(NORG) 53 NHAF=NORG+[R(HAF/0.005) 54 W=WLINE 55 TENFAC=PHASE*WEIGHT/TENS 551 IF (KSHAPE) 611,56,611 56 TA=-16.*(W*#3) 57 TR=3.*(W**2) 58 DO 61 [=1,NGEN 59 XI=I 60 XA=(XI+0.005)-ORIGIN 61 YA(1,1)=(TENFAC*TA*XA)/((4.*(XA**2)+T8)**2) 610 GO TO 62 611 TA= -(W++2) 612 DO 615 1=1,NGEN 613 XI=I 614 XA=(XI*0.005)-ORIGIN 615 YA(1,1)=TENFAC*(XA/TA)*EXPF((XA**2)/TA) 62 LENGTH=NGEN 63 NY=1 64 IF. (NA) 112,112,65 65 DC 111 K=1,NA 66 NEQ=NQA(K) 67 KUPL=A(K)/0.005 68 LENGTH=LENGTH+(NEQ*KUPL) 69 LENGTH=XMINOF(LENGTH, NHAF) 70 AK=A(K) 71 DO 106 I=1,LENGTH \ 72 GO TO (76,75,74,73),NEQ 73 I4=I-IR(4.*AK/.COS) 74 I3=I-IR(3.*AK/.005) 75 12=I-IR(2.*AK/.005) 76 []=I-IR(AK/.005) 77 YPLUS=0.0 78 GO TO (79,82,87,94),NEQ 79 IF(I1) 102,102,80 80 YPLUS=YA(NY, 11) 81 GO TO 102 82 IF. (I1) 102,102,83 83 YPLUS= 2. * YA(NY, 11) 84 IF (12) 102,102,85 85 YPLUS= YPLUS+YA(NY, 12) 86 GO TO 102 87 IF (I1) 102,102,88 88 YPLUS=3.*YA(NY,I1) 89 IF (12) 102,102,90 90 YPLUS=YPLUS+3. #YA(NY,12) 91 IF (13) 102,102,92 92 YPLUS=YPLUS+YA(NY,I3)

93 GO TO 102-

94 IF (I1) 102,102,95

 \tilde{j}

95 YPLUS=4.*YA(NY,11) 96 IF (12) 102,102,97 97 YPLUS=YPLUS+6.#YA(NY,I2) 98 IF (13) 102,102,99 99 YPLUS=YPLUS+4.*YA(NY,13) 100 IF (14) 102,102,101 101 YPLUS=YPLUS+YA(NY, 14) 102 GO TO (105,103),NY 103 YA(1,1)=YA(2,1)+YPLUS 104 GC TO 106 105 YA(2,1) = YA(1,1) + YPLUS106 CONTINUE 107 GG TO (108,110),NY 108 NY=2 109 GO TO 111 110 NY=1 111 CONTINUE 112 IF (N8) 165,165,113 113 DO 164 K=1,NB 114 NEQ=NQB(K) 115 KUPL=0(K)/.005 116 LENGTH=LENGTH+2*NEQ*KUPL 117 LENGTH=XMINOF(LENGTH, NHAF) 118 BK=B(K)119 DO 159 I=1,LENGTH 120 GC TO (125,123,121),NEQ 121 I6=I-IR(6.#BK/.C05) 122 I5=I-IR(5.*BK/.005) 123 I4=I-1R(4.*8K/.COD) 124 I3=I-IR(3.*8K/.005) 125 I2=I-IR(2.*8K/.005) 126 I1=I-IR(BK/.005) 127 YPLUS=0.0 128 GO TO (129,134,143),NEQ 129 IF (I1)155,155,130 130 YPLUS=YA(NY, 11) 131 IF (I2) 155,155,132 132 YPLUS=YPLUS+YA(NY,I2) 133 GO TO 155 134 IF (11) 155,155,135 135 YPLUS=2.*YA(NY,I1) 136 IF (I2) 155,155,137 137 YPLUS=YPLUS+3.*YA(NY,12) 138 IF (13) 155,155,139 139 YPLUS=YPLUS+2.*YA(NY,I3) 140 IF (I4) 155,155,141 141 YPLUS=YPLUS+YA(NY,I4) 142 GO TO 155 143 IF (11) 155,155,144 144 YPLUS=3. #YA(NY,II) 145 IF (12) 155,155,146 146 YPLUS=YPLUS+6.*YA(NY,12) 147 IF (13) 155,155,148 148 YPLUS=YPLUS+7. +YA(NY,13) 149 IF (14) 155,155,150 150 YPLUS=YPLUS+6. +YA(NY,14)

151 IF (15) 155,155,152 152 YPLUS=YPLUS+3. *YA(NY,15) 153 IF (16) 155,155,194 154 YPLUS=YPLUS+YA(NY,16) 155 GC TO (158,156),NY 156 YA(1,1)=YA(2,1)+YPLUS 157 GO TO 159 158 YA(2,I)=YA(1,I)+YPLUS 159 CONTINUE 160 GU TO (161,163),NY 161 NY=2 162 GC TO 164 163 NY=1 164 CONTINUE 155 IREAD=NHAF+1 166 DO 168 I=1,NHAF 167 IREAD=IREAD-1 168 YA(3,I)=YA(3,I)*YA(NY,IREAD)169 IF (NHAF-NHAFMX) 172,172,170 170 NHAFMX=NHAF 171 NORGMX=NORG 172 IF (NSPEX-NSPEC) 173,173,17 173 YMAX=0.0 174 DO 178 I=1, NHAFMX 175 YY = YA(3, I)1751 YY=ABSE (YY) 176 IF (YY-YMAX) 178,178,177 177 YMAX=YY 178 CONTINUE 179 DO 180 I=1,NHAFMX AMULT = HIY/(2.0*YMAX)180 YA(3,I) = AMULT*YA(3,I) + 5.01806 GRALN=FLOATF(NHAFMX) #0.005#(1.0/GPI)+1.0 STATEMENTS 9014-9018, 9011 LETTER THE PROBLEM NAME ACROSS THE TOP OF THE GRAPH 9014 LETHIT=XF1XF(10.0*GRALN/72.0) 9015 IF(LETHIT-4) 9017, 9017, 9016 9016 LETHIT = 49017 [F(LETHIT) 9018, 9018, 9003 9018 LETHII=1 9003 CALL SETGPH(GRALN, 10.0, 0.50) 1406 IF (LETTER) 9004, 9012, 9004 9004 CALL FRAME (0.10, 0.10) 9005 DO 9007 I=1,3, 2 9006 CALL XLN(C.O, GRALN, FLOATF(I), O.C) CALL XLN (GRALN, C.U, FLOATF(I + 1), O.G) 9007 CONTINUE DU 1111 I = 5, 8, 2CALL XLN (0.0, GRALN, FLOATF(1), 0.0) CALL XLN (GRALN, G.C, FLOATF(1 + 1), 0.0) 1111 CONTINUE SOLZ JEND = XFIXF(GRALN) - 1 1407 IF (LETTER) 9008, 9011, 9008

С

С

9008 DO 9010 I=1, JEND, 2

9009 CALL YLN (0.0, 10.0, FLOATF(I), 0.0)

> CALL YLN(10.0, C.0, FLOATF(I + 1), 0.0)

-102-

	CONTINUE			
30107	$T_{C} = 2\pi (16 \times 0.21) + 112 = 1112 + 9011$			
	$\frac{1}{2} \frac{1}{2} \frac{1}$			
0011	CALL ILN(0.0, 10.0, FLOAT (GLAD) IT (0.0)			
9011	$\begin{array}{c} \textbf{CALL LIK(0.0), 10.1}, \textbf{Lenging 0}, \textbf{ANANEY} \\ \textbf{True Transformed and 1000, 0001} \end{array}$			
1408	THE LECTERT SUUL, 1409, SUUL CANTCHENTE DOCT DEST OF THE LE	TTERTNG BUT	NONE DE	тне
L A	STATEMENTS SUUL-8023 PUT THE REST OF THE CU	TESTROY COT		
C	HOLERITH NUMBERING, UN THE GRAPH			
8001	IF (KSHAPE) 1001, 1002, 1001			
81001	ALPHA(1) = 011030272154			
8	ALPHA(2) = 626231214560			
P.	ALPHA(3) = 433145256230			
8	ALPHA(4) = 214725606060			
8002	CALL LTR(GRALN + 1.0, 10.3, 1, 0, ALPHA)			·
8003	60 TO 1003			
81002	ALPHA(1) = 020030434651			
8	ALPHA(2) = 254563713121			
`В	ALPHA(3) = 456043314525			
8	ALPHA(4) = 623021472560			
8004	CALL LTR (GRALN + 1.0, 10.3, 1, 0, ALPFA)			
81003	ALPHA(1) = 031030504651			
8	ALPHA(2) = 317146456321			
в	ALPHA(3) = 436062232143			
в	ALPHA(4) = 251360006060			
В	ALPHA(5) = 606060272164			
B	ALPHA(6) = 626260472551			
8	ALPHA(7) = 603145233060			
8005	CALL LTR (GRALN + 1.0, 10.1, 1, 0, ALPHA)		۰.	
5001	CALL LTRNUM (GPI, GRALN + 2.7, 10.1, 1, 0)			
5006	CALL LTRNUM (HIY, GRALN + 2.3, 9.9, 1, 0)			
в	ALPHA(1) = 031130432151	•		
8	ALPHA(2) = 272562636043			
В	ALPHA(3) = 314525136060			
ß	ALPHA(4) = 606060606031	4		
B	ALPHA(5) = 452330256260	1		
8	ALPHA(6) = 472521421463			
8	ALPHA(7) = 461447252142			•
8006	CALL LTR (GRALN + 1.0, 9.9, 1, 0, ALPHA)			
8007	IF(NSPEX-1) 8008, 8013, 8008			
8008	CALL YLN (0.0, 10.0, GRALN + 7.0, 0.0)		•	
8009	CALL YLN (0.0, 10.0, GRAEN + 22.0, 0.0)			
вĴ	ALPHA(1) = 030730634646			
8	ALPHA(2) = 604421457060			
8	ALPHA(3) = 624725233125			
8	ALPHA(4) = 626063466043			
в	ALPHA(5) = 256363255160			
8	ALPHA(6) = 314547646360			
в	ALPHA(7) = 242163216060			
8010	CALL LTR (GRALN + 9.0, 5.6, 3, 0, ALPHA)			
8	ALPHA(1) = 021030526321			
в	ALPHA(2) = 474325506370			
B	ALPHA(3) = 472524603145			
в	ALPHA(4) = 476463602421		· · · ·	
B	ALPHA(5) = 632160302551			
B	ALPHA(6) = 256060606060			
8011	CALL LTR (GRALN + 8.8, 6.2, 3, 0, ALPHA)	• .		
8012	GO TO 1004			

8013 CALL LTR (GRALN + 1.0, 9.0, 1, 0, BNAME) 8014 IF(NA) 7001,8018,7001 7001 WIDTH =' GRALN + 2.0 7002 DEPTH = 8.88015 DO 8017 I = 1, NA 7003 IF(DEPTH - 1.0) 7004, 7004, 7006 7004 DEPTH = 8.87005 WIDTH = WIDTH + 6.0 7006 DEPTH = DEPTH - 0.2 ALPHA(1) = 0402305060608 в ALPHA(2) = 255064316521ALPHA(3) = 432545637360В ALPHA(4) = 3113003305738 ALPHA(5) = 606631633050Б B ALPHA(6) = 211360006000ALPHA(7) = 606060602721R ALPHA(8) = 6462526060508 8016 CALL LTR (WIDTH, DEPTH, 1, 0, ALPHA) 1201 CALL BINCON (HOLD) 1202 WRITE OUTPUT TAPE 3, 1203, NQA(I) 1203 FORMAT (16) $B1204 \ SCALE(1) = 606060606630$ 1205 SCALE(2) = HULD(1) 1206 CALL LTR (WIDTH - 0.4, DEPTH, 1, 0, SCALE) 1207 CALL LTRNUM (A(I), WIDTH + 3.0, DEPTH, 1, 0) 8017 CONTINUE 8018 IF(NB) 8019, LOC5, 8019 8019 DO 8021 I=1,NB 7007 IF (DEPTH - 1.0) 7008,7008,7010 7008 DEPTH = 8.87009 WIDTH = WIDTH + 6.0 7010 DEPTH = DEPTH - 0.21 8 ALPHA(1) = 040230606050ALPHA(2) = 2550643165218 ALPHA(3) = 432545637360B ALPHA(4) = 311301330073ß Б ALPHA(5) = 606631633060 ALPHA(6) = 211360606060В ALPHA(7) = 6060606027218 ß ALPHA(8) = 6462626060608020 CALL LTR (WIDTH, DEPTH, 1, 0, ALPHA) 1301 CALL BINCON (HOLD) 1302 WRITE OUTPUT TAPE 3, 1203, NQB(I) 81304 SCALE(1) = 60606060630 1305 SCALE(2) = HOLD(1) 1306 CALL LTR (WIDTH - 0.4, DEPTH, 1, 0, SCALE) 1307 CALL LTRNUM (8(1), WIDTH + 3.0, DEPTH, 1, 0) 8021 CONTINUE B1005 ALPHA(1) = 020330433145 Б ALPHA(2) = 2566312463308 ALPHA(3) = 13006000606008 ALPHA(4) = 606060272164ALPHA(5) = 6262606060608 8022 CALL LTR (GRALN + 1.1, 8.8, 1, 0, ALPHA) 1106 CALL LTRNUM (WLINE, GRALN + 2-1, 8-8, 1, 0) 8023 CALL YLN (0.0, 10.0, WIDTH + 8.0, 0.0)

```
-104-
```

```
81004 ALPHA(1) = 053000330000
   ALPHA(2) = CO606060606060
в
6001 CALL LTR (-0.05, 0.25, 1, 1, ALPHA)
     JEND = JEND + 1
 6002 DC 6005 I=1, JEND
6003 BER = FLOATF(I)*GPI
6004 CALL LTRNUM (BER, FLOATF(1) +0.15, 0.15, 1, 1)
6005 CONTINUE
1419 GO TO 9013
 1409 IF (KSHAPE) 1410, 1412, 1410
1410 WRITE OUTPUT TAPE 3, 1411
1411 FORMAT ( 19H GAUSSIAN LINESHAPE )
1418 GO TO 1414
1412 WRITE DUTPUT TAPE 3, 1413
1413 FORMAT ( 21H LORENTZIAN LINESHAPE )
1414 WRITE OUTPUT TAPE 3, 1415, GPI
1415 FORMAT ( 20H HORIZONTAL SCALE = , F12.6, 15H GAUSS PER INCH )
1416 WRITE DUTPUT TAPE 3, 1417, HIY
1417 FORMAT ( 16H LARGEST LINE = , F12.6, 20H INCHES PEAK-FO-PEAK )
'9013 CALL CURVE(0, 0, 0.0, 0, 0.0, GRALN, 0.0, 10.0, 1)
1801 DO 1805 I=1, NHAFMX
1802 XPT = 1.0/GP1*0.005*FLOATF(1)
1803 \text{ YPT} = YA(3, I)
1804 CALL PLOTPT(XPT, YPT)
1805 CONTINUE
 230 GO TO 3
 231 CALL NDPLOT
 232 CALL EXIT
      END
```

17

* LABEL
1 FUNCTION IR(X)
2 Y=INTF(X)
3 D=ABSF(X-Y)
4 IF (D-.5) 5,7,7
5 IR=Y
6 RETURN
7 IF (X) 8,10,10
8 IR=Y-1.
9 RETURN
10. IR=Y+1.
11 RETURN

END

8

LABEL SUBROUTINE LTRNUM (ANUM, XBEG, YBEG, LHIGH, LINE) DIMENSION SCALE(2), HOLD(22) 1 CALL BINCON (HOLD) 2 WRITE OUTPUT TAPE 3, 3, ANUM 3 FORMAT (F6.3) 4 SCALE(1) = 6060606606630 5 SCALE(2) = HOLD (1) 6 CALL LTR (XBEG, YREG, LHIGH, LINE, SCALE) RETURN END

APPENDIX II

-105-

Fortran IV Computer Program MO

The four different molecular orbital calculations described in chapter four were performed with the Fortran IV program package MO. This program will perform a Huckel LCAO calculation (with or without overlap) or a McLachlan SCF calculation depending on the values of the input data. It will also calculate methyl, methylene, or ring coupling constants from the calculated wavefunctions.

The heart of the program is the SHARE subroutine HDIAG which performs the matrix diagonalizations. The routine has been changed from Fortran II to Fortran IV and the statements from 1000 through 1001 inclusive have been added but other than that the routine is unchanged. The subroutine METHYL contains the formulae for calculating the methyl and methylene coupling constants and the date on which these formulae were last changed. The date appears on the output and allows one to easily keep track of which formulae were used in any given calculation. The subroutines XEMERR and SETFPT are monitor subroutines which supress the error comments which are ordinarily printed out on underflows. These routines are specifically designed for the LRL 7044 IBSYS monitor⁸⁶ and may be superfluous or undefined with a different monitor.

The input data for a single calculation consists of two control cards and the input H and S matrix cards. The first card contains the name of the molecule and has the format 12A6. The second card defines . the type of calculation and contains the following data fields:

CONTENTS

I2

FIELD

ALAM

Ν

F6.3

F6.3	Q
12	IORBIT
8(412)	(IH(I), IC(I), ICPRM(I), ICDPRM(I), I = 1,8)
The definitions of these input	it variables are as follows:
N	The order of the H and S matrices.
ALAM	The value of lambda in the McLachlan SCF calculation: If zero, no McLachlan cal- culation is performed.
Q	The value of the sigma-pi interaction parameter from which ring coupling con- stants are calculated. If zero, ring coupling constants are not calculated.
ÍORBIT	The orbital of the odd electron in the radical cation. If zero, IORBIT is assumed to be N/2 if N is even, N/2 - $\frac{1}{2}$ if N is odd.
IH(I)	The number of the hydrogen atom in the Ith methyl or methylene group.
IC(I)	The number of the carbon atom in the Ith methyl or methylene group.
ICPRM(I)	The number of the carbon atom to which the Ith methyl or methylene group is attached.
ICDPRM(I)	The number of the second carbon atom to which the Ith methylene group is attached. If the Ith group is a methyl this is left blank or set equal to zero.
As stated, all of this info	rmation goes on a single card whose format

-106-

statement is (12, 2F6.3, 3612).

After the two control cards there follows the stack of cards giving the input H-matrix. Each non-zero matrix element H_{ij} is listed on a separate card with format (214, F 64.10). The first two fields contain the values of I and J respectively and the third field contains the value of the matrix element. At the end of the H-matrix deck a blank card is inserted. If an overlap calculation is to be done the S-matrix deck follows the H matrix deck in the same manner. Only the off-diagonal overlap elements need be given. If the calculation is to be done neglecting overlap a blank card is inserted in place of the overlap deck. Of course when doing a McLachlan calculation there must be no overlap deck.

As an example of the use of this program we consider an overlap calculation performed on the molecule 2-methylcyclohexadiene-1,3 using the parameters of Coulson and Crawford. We wish to do a Huckel calculation both with and without overlap and a McLachlan calculation with lambda equal to 1.0. Further we wish to calculate all methyl and methylene coupling constants and all unsaturated proton coupling constants assuming a Q of 20.0. The numbering of the atoms is shown in Fig. 20. The data cards will appear exactly as shown below, where - represents a blank space.

2-METHYLCYCLOHEXADIENE-1, 3. SAMPLE CALCULATION.

10--1.00--20.0---8-7-2--10-5-4-6-9-6-5-1

---8-----0.5

---6---9----2.00

-107-



MU-35086

Fig. 20

---7---8-----2.00

---3---1.00

---2---3----1.00

---1---2----1.00

blank

blank

2-METHYLCYCLOHEXADIENE-2,3. OVERLAP CALCULATION. 10-----20.0---8-7-2--10-5-4-6-9-6-5-1 ---8-----0.5 ---9-----0.5 --10--10-----0.5 ---7----0.1 ---6----0.1 ---4---5----0.76 ---5---6----0.76 ---1---6----0.76------2---7----0.76 ---5--10----2.00 4--6---9----2.00 ---7---8----2.00 ---3---4----1.00 ---2---3----1.00 ---1---2----1.00 blank ---4---5----0.19

----1----6-----0.19 ----2----7----0.19 ----5--10-----0.50 ----6----9-----0.50 ----7---8-----0.25 ----2---3----0.25 blank blank

blank

The listing of the Fortran program is as follows:

\$10 \$10	400721,MU,20,LEVY B	·
SIGFT	C MO	
C	HUCKEL MOLECULAR ORBITAL GALCULATION INCLUDING OVERLAP	
Ċ	THIS PROGRAM REQUIRES THE SUBROUTINGS HOLAG, MULT, MCTHYL, AND XEMI	RR
-	DIMT NSIGN 11(41,41), U(41,41), ANAME(12), NUM(41), K(41), S(41,41),	
	1C(4),41), 1((4), 1H(4), 1CPRM(9), 1CDPRM(9), CHKRU(41), HP(41,41)	
	COMMENTE AN ACTION ACTOR CONST. MENTE DAY, LYEAR	•
	Control (C)	
~	- GALE PETHTE - The eratements on a to and tachterne and set "WEDVIHING" (MDDDTAN)	TO 7500
С. 	THE STATEMENTS DUVIE IN AND TRECOPTING SOUL STATEMENTS TREORING	IU ZEKU
101		
	CHKRO(1) = 50.0	
102	NUM(I) = I	4000080
1	DO[3][I] = 1,41	
2	DO 3 J = $1,41$	•
	HP([,J) = 0.0	
3	H(I,J) = 0.0	4000116
	ICARDS = 0	
	DC = 3001 I = 1.41	
	DO(360) I = 1.41	
	IE(1-1) SECC. SEC1. 5860	
5800	S(1, 1) = C(0)	
2000		
6001		
2001		· ·
5001		
. L	THE STATEMENTS DURN TE SUCA READ ARD FRINT THE TRIOT BATRICES	4000160
4	$READ = \{2, 5\} \{A_{N,4} \in \{1\}, 1 = 1, 12\}$	4000100
5	FURMAT (12A6)	4000100
6	READ(2,7)N, ALAM, Q, ICRUIT, (IH(I), IC(I), ICPAP(I), ICPAP(I), ICPAP(I), I=1,8)	
7	FORMAT(12,2F6.3, 3612)	
8	IF(N) 15, 55, 15	4000190
15	WRITE $(3, 16)(ANANE(1), 1 = 1, 12)$	4000200
801	WRITE (J,802)	4000210
802	FORMAT (1HO, 10X, 39HNCN-ZERD ELEMENTS IN ORIGINAL H-MATRIX	4000220
. 9	READ (2,10) I, J, HCLU	4000230
10	FORMAT (14, 14, Fo4,16)	4000240
11	1F(1) 12, 3002, 12	4000250
12	H(J, J) = H0L6	4000260
	HP(f,J) = HOLD	
	H(1, 1) = H(1, 1)	4000270
	$(\mathbf{r}_{i},\mathbf{r}_{j}) = (\mathbf{r}_{i},\mathbf{r}_{j})$	
1 26 1		4000286
1201	$\frac{1}{2} = \frac{1}{2} = \frac{1}$	4600290
1242	$\frac{1}{1000} \frac{1}{1000} \frac{1}{1000} \frac{1}{1000} \frac{1}{1000} \frac{1}{1000} \frac{1}{1000} \frac{1}{10000} \frac{1}{10000} \frac{1}{10000000000000000000000000000000000$	4000200
13		4000 300
3002	READ(2, 10) 1, J, HLLD	
	IF (H0[D-L1- I-0CL-05) GO 10 3029	
	WRIIE(3, 3003)	
	ALAM = 0.0	
	GG FU 3006	
1		
3003	FORMATCHO, LOX, SCHNON-ZERO OFF#DIAGONAL ELEMENTS IN ORIGINAL S-M	
3004	READ (2,10)I, J, HOLU	4000336
3005	IF(I) 3006,14,3005	4000340
		•

- p.
- --

	. •	
3006	$S(I,J) \approx H(J)$	4000350
	S(1) (1) $=$ $S(1)$ (1)	4060366
1007		4000376
3007	WRITE (3, 5008)1, 3, 3(1,3)	
	ICARDS = ICARDS + I	4000380
3008	FORMAI(LSX, 2HS(,12,1H,,12,4H) = , F9+5)	4000300
3069	60 10 3004	4000390
C	THE STATEMENTS COWN TO 3033 DO THE ACTUAL CALCULATION	
14	CALL HDIAG (5, N, O, U, NR)	4000400
16	FORMAL (30HI NOLECULAR ORBITAL CALCULATION OF , 1246)	
3016	WRITE (3.3011)	4000430
3011	$\left\{ c_{0} \right\} = \left\{ c_{0} \right\} = $	4000440
2012		4000450
2012		4006460
	WE LEE () JULTIAL ALJOINT ALL JULTIAL AND ALL AND AL	4000470
3014	FURNALLIDAY ZHOY, 12, 10, 12, 40, 5, 70, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7,	4000480
- 3015	01 3016 1 =1, \	4000400
3616	S(1,1) = S(1,1)ee(-0.5)	4000490
3017	CALL MULT(U,S,G,N)	4000500
	NERD = N-L	4000510
3018	DC 3022 I = I, NERD	4000520
	NIRO = I + I	4000536
3019	$00^{\circ} 3022 J = NIRO + N$	4600540
- 3020	$\Theta(L) = H(L, 1)$	4000556
2020		4000560
3021		4000570
3022		4000580
3023		4000590
3024	CALL MULI(S,H,C,N)	4000000
3025	CALL (ULF(C,S,H,M)	2000000
3029	CALL HDIAG(H,N,C,U,NR)	4000010
3033	CALL HULT (S+U+C+N)	4000620
18	WRITE (3,19)	400050
19	FORMAL (ING, ICX, 92HENERGY = ALPHA + (LAMBOA)(BELA). ALGEORAICAL	4000660
	11Y LARGEST LAMBOA CORRESPONDS TO LOWEST ENERGY.)	4000670
	IF(IC4805) 3034. 22. 3034 7	
3634	WRIFE (3.3035)	4006630
2021	CONVERTING SX. ISBOCOLS CREITALS	
,	THE STATEMENTS TO AND ORDER THE EIGENVECTORS IN ORDER OF INCREASING	G ENERGY
- Le - 10 - 10	THE STATEMENTS TO SSA OVER THE EXCEPTION OF THE PERIOD	4000680
22		4000690
23	K(1) = 1	4000700
231	ISTOP = N - I	4000716
24	DC 34 I = 1, IS107	4000710
25	IST = I + I	4000720
26	-00 34 J = IST, N	4000730
27	IF (H(I,1) - H(J,J)) 20, 34, 34	4000746
28	ATFMP = H(I,I)	4000750
29	I1FMP = K(I)	4000760
30	$H(I \bullet I) = H(J \bullet J)$	4000770
31	K(1) = K(1)	4000786
	(A + A + A) = A T A M B	4000790
24		4000800
د د		4000816
- 34	CONTINUE.	4000820
35	NEND = 2*(0/2)	4000020
. 351	00 45 I = 1, NEND, 2	-0000000
C	THE STATEMENTS TO 4512 WRITE OUT THE ENERGIES AND WAVE FUNCTIONS	
36	WRITE $(3,37)H(1,1)$, $H(1+1, 1+1)$	4000840
37	FORMAL (180, 9%, 108 LAMBDA = , FILS, 35X, 98LAMBDA = , F1LS)	4000850
38	DO 45 J = 1, \aleph	4000860

-112-

* .

-113-

39	INDA = K(1)		4000870
40	INDB = K(1 + 1)		4000880
4.1	$\Delta H = H (1 + 1 N h \Lambda) + + 2$		4000890
	N(0, 0) = 0(1, 1, 1)(0, 1) + 2		4000900
42			A000010
43	WRITE (3,44)NCM(J), U(J,INDA), NOA(J), RHUA,	NUMBER OF STREET	4000910
	I INDB), NUM(J), RAGB		4000920
44	FORMAT (14X, 3H C(, 12, 2H)= , F8.5, 7X, 4hRHU(, 12,	2H)- ,F8.5,	4000930
	117X, 3H C([, 12, 2H)= , F8.5, 7X, 4HRHC(, 12, 2H)= ,	F8.5)	4000940
. 45	CONTINUE		4000950
46	IE(N-VEND) 47. 17. 47		
1.7	LATTE (A.GRIH(M.N)	•	4000970
	$\frac{1}{2} \left(\frac{1}{2} + 1$		4000980
	$\int O(\mathbf{r} + \mathbf{r} + r$	· · ·	4000990
49			4001000
50	INDA = K(N)		4001000
501	$RHUA = U(J, INDA) \ast \ast Z$		4001010
51	wRITE (3,512)NUM(J), U(J, INDA), NDM(J), RHCA		4001020
512	FORMAL (14X, 3H C(, 12, 2H)= , $FS_{*}S_{*}$ 7X, 4HRHO(, 12,	2H)= ,F8.51	4001030
17	IF(ICARUS) 9001, 52, 9001		
90C1	WRIFE(3,9002)	1.	
9002	FORMATCING, 5X, 20HERANSFORMED ORBITALS)		
4351	00.4045 I = 1. NECO. 2		4001040
4036	WRITE (3.4037)H(1.1), H(1+1, (+1))		4001050
10.00	$\frac{1}{2} \frac{1}{2} \frac{1}$	= . E11.5)	4001060
4037	$\frac{1}{2} \frac{1}{2} \frac{1}$	- , ,	4001000
40.58	DU 4040 J# L, N		4001070
4039	INDA = K(1)		4001080
4040	INOB = K(I + 1)		4001090
4041	RHGA = C(J, INDA) * *2		4001100
4042	RHOB = C(J, INDB) * *2		4001110
4043	WRITE (3.4044)NLM(J), C(J,INDA), NUM(J), RHOA,	NUM(J), C(4001120
	1.1 + 1.53B) + $NUM(L)$ + $RIOB$		4001130
4044	508MA1 (14X, 3H C(, 12, 2H)= , F8.5, 7X, 4HRH0(, 12,	2H)= .F8.5.	4061140
	(1)	E8.5)	4001156
1015	$\frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}$	1 0 • 2 1	4001160
4045			4001176
4046	17 (N-NEND) 4047, 52, 4047		4001170
4047	WRITE (3,4048)H(N,N)		4001180
4048	FORMAT (1HO, $3X$, 1CH LAMBDA = , FI1.5)		4001190
4049	DC 4011 J = 1, N	•	4001200
4050	INDA = K(K)		4001210
4501	RHOA = C(J, INDA) * * 2	11 A.	4001220
4051	WRITE (3.4512)NUM(J), C(J, INLA), NUM(J), RHOA		4001230
4512	EORMAL (14X, 3H C(, 12, 2H)= , F8, 5, 7X, 4HRH0(, 12,	2H)= •F8•5)	4001240
5.2		.	4001256
52	- ΕΠΟΝΑΤ /186 - ΤΛΥ, ΟΦΗΜΕΜΑΖΟ ΔΕ Ο ΗΥ Ο ΒΕΤΑΤΙΟΝΆ # - ΙΙ)	
در . -	FURNING A LINCE LOAD ZOUNDER OF Z OF Z NUTHEROND $=$ \mathbf{y} to	NUTANES	
	THE STATEMENTS NUMBERED GUOD CALCULATE THE COOPLING CL	(21) AVA 1 3	
6001	TEST = 1.002 - 05		
6002	IF(Q.GT.TEST) GC TO 3900		
6003	IF(IH(1)) 5900, 54, 5900		•
5900	WRITE (3, 5901)		
5961	FORMAT(ING,////, 10x, 78HTHE COUPLING CONSTANTS LISTED	BELOW ARE BA	
	ISED ON THE FOLLOWING ASSUMPTIONS,)		
5902	IF(0.LT.FEST) GC TG 5905		
5903	WRITE(3. 5904) C	•	
SUCA	EORMA1(15X,380) = E5.2)		· .
5016	100000111200000 = 7.1000000000000000000000000000000000000		
5900	UU 2712 1 - 490		
	16/16/1111 6007 6/17 4007		
2460	IF(IH(I)) 5907, 5914, 5907		

```
5908 WRITE (3, 5909) IH(1), IH(1), IC(1), ICPRM(1), ICDPRM(1)
5909 FORMAT(15X,2HA(, 12, 49H) IS DUE TO A METHYLENE GROUP (HYDROGENS N
    TUMBERED, 13, 17H, CARBON NUMBERED, 13, 21H) ATTACHED TO CARBONS,
    213, 4H AND, 13, Lt.
                            )
5910 GO TO 5913
5911 WRITE(3, 5912) IH(1), IH(1), IC(1), ICPRM(1)
5912 FORMAT(15X,2HA(, 12, 46H) IS DUE TO A METHYL GROUP (HYDROGENS NUMB
    IERFO, 13, 17H, CARBON NUMBERED, 13, 20H) ATTACHED TO CARBON, 13,
    218.
             ۱.
5913 CONTLINE -
5914 IF(IH(1)) 5600, 6(64, 5600
5600 WRITE(3, 5915) MUNTH, IDAY, IYEAR
5915 FORMAT(15x, 93HMETHYL AND METHYLENL COUPLING CONSTANTS CALCULATED
    IWITH THE FURMULAE IN SUBROUTINE METHYL CN , 12, 14/, 12, 14/, 12, 14/ )
6004 00 6039 11 = 1.2
     00.6040 I = 1.41
6040 \text{ CHKRO(I)} = 50.0
     IF(IORBIF)6028, 6065, 6028
6005 \text{ NORR} = N/2 - 1 + 11
     GC TC 6006
6028 NOR8 = IORCIT - 1 + II
60C6 INDA = K(NORB)
6007 [F([1 - 1) 6011,6008,6011
2008 WPITE(3, 6009)
6009 FORMAT(ING, 10X, 34HPOSITIVE ICN COUPLING CONSTANTS
6010 GO TO 6613
6011 WRITE(3, 6012)
6012 FORMAT(ING, 10X, 34HNEGATIVE ION COUPLING CONSTANTS
                                                                  )
6013 DG 6031 I = 1,8
6014 IF(IH(I)) 6015, 6-32, 6015
6015 IA = 1H(I)
6016 I8 = 10(1)
                                               2
6017 ID = ICPRM(1)
6018 IE = ICDPRM(I)
6019 \text{ NUM}(1A) = 0
     NUM(13) = 0
6020 \text{ AH} = U(IA, INDA)
6021 \text{ AC} = C(18, INDA)
6022 \text{ ACP} = C(ID, INDA)
6023 IF(IE) 6024,6025,6024
6024 ACUP = C(IE, INDA)
6025 CALL METHYL
6026 WRIFE(3, 6027) IA, CONST
6027 FORMAT(15X, 2HA(, 12, 4H) = , F8.3, 6H GAUSS
                                                           )
6031 CONTINUE
6032 IF(G.LT.TEST) GC TO 6039
6033 DO 6039 I = 1,N
6034 IF(NUM(I)) 6035, 6039, 6035
6035 DC 6036 J = 1,N
6036 IF((A0S(U(1, INDA) #*2-CHKRC(J))).LT.TEST) G0 T0 '60'39
6037 CFKR0(I) = U(1,INUA)**2
6038 CONST = ABS(CHKRO(I)+C)
     WRITE(3,6027) I, CONST
6039 CONTINUE
  54 IF(ALAM.LT.TEST) GG TO 101
```

WRITE (3,433) ALAM

```
IF(Q.NE.0.0) WRITE (3,434) Q
    CONTINUE
400 IF(IOUBIT.EQ.0) IORBIT = N/2
402 CONTINUE
404 DO 407 I = 1,N
405 \text{ INDA} = \text{K(I)}
406 \ 00 \ 407 \ J = 1.N
407 C(J,I) = U(J,INDA)
403 DC 443 105 = 1,2
WRITE(3,435) 10RBIT
    DC - 460 I = 1, W
    DO 460 J = 1,N
460 H(I,J) = HP(I,J)
408 00 409 1 4 1 N
409 H(I,I) = H(I,I) + 2.0*ALAM*(C(1,IORBIT)**2)
410 CALL HOIAG(H,N,C,U,NR)
411 DC 412 I = 1,4
412 K(I) = I
413 DO 423 I = 1,ISTOP
414 \text{ IST} = I + I
415 DU 423 J = IST, N
416 IF(H(I,I) - H(J,J)) 417, 423, 423
417 \text{ AIEMP} = H(I,I)
418 ITEMP = K(I)
419 H(I,I) = H(J,J)
420 K(I) = K(J)
421 H(J,J) = ATEMP
422 K(J) = ITEMP
423 CONTINUE
424 DG 427 1 = 1.N
425 \text{ INDA} = K(1).
426 UC 427 J = 1.N
427 S(J,I) = U(J,INDA)
428 DG 442 I = 1.N
429 RC = C(I,IURBIT) **2
430 | JSTCP = ICREIF - 1
431 DC 432 J = 1, JSTUP
432 RO = RO + S(1,J)**2 - C(1,J)**2
433 FORMAT(1H0,////,1CX,4CHMCLACHLAN SCF SPIN DENSIFIES ASSUMING, ,/,
   1 15X, 9HLAMBDA = , Fo.3)
434 FORMAI(15X, 4H0 = , F0.3)
435 FORMAT(1H0, 10X, J4HUNPAIRED ELECTRON IN CRHIT NUMBER , [2]
    ACUP = ABS(Q*RO)
436 15(0) 437, 440, 437
437 WRITE(3, 438) 1, PG , I, ACUP
438 FORMAI(15X_{4}HRHO(,I2_{4}H) = F8.5_{10}X_{2}HA(,I2_{4}H) = F0.5_{0}HGAUSS)
439 GO TO 442
440 WRITE(3, 441) 1, 80
441 FORMAT(15X, 4HRHO(, 12, 4H) = , F6.5)
442 CONTINUE
4+3 ICRBI1 = ICRBIT + 1
    GO TO 101
                                                                              4001280
 55 WRITE (3,56)
 56 FORMAT (9HIFINISHED )
                                                                              4001290
                                                                              4001300
 57 CALL EXIT
                                                                              4001310
    END
```

SIBFTC MULT	· .
SUBROUTINE MULT(A, B, C, N)	0010
DIMENSION A(41,41), B(41,41), C(41,41)	
1 GG 5 I=1,N	0040
2 D0 5 J=1,N	0050
3 C(1, J) = 0.0	0060
4 DC 5 L≠1,N	0076
5 C(1,J) = C(1,J) + A(1,L) * H(L,J)	0800
6 RETURN	5635
END	- C10C

\$18FTC XEMERR SUBROUTINE XEMERR(ERRNO) INTEGUR ERRNO IF(30-ERRNO) 100, 1, 100 1 CALL £XEM(71,1) GO TO 1000 100 CALL 1XEM(71, C) 1000 RETURN

ENC

\$IBFTC METHYL SUBROUTINE METHYL COMMUNE IE, AH, AC, ACP, ACDP, CONST, MENTH, IDAY, IYEAR STATEMENTS 6-8 GIVE DATE ON WHICH FORMULAE WERE LAST CHANGED С 6 MONTH = 127 10AY = 118 IYEAR = 64 1 IF(IE) 2, 4, 2 STATEMENT 2 IS THE FORMULA FOR CALCULATING A NETHYLENE COUPLING CONSTANT C 2 CONST = ABS(327.0 «AH##2 + 161.0 * 4C # AH + 19.8 # AC##2 + 1(5.95.* AH + 1.46 # AC) # (ACP + ACDP) - 2.78*(ACP##2 + ACDP##2)) 3 GC TO 5 С STATEMENT 4 IS THE FORMULA FOR CALCULATING A METHYL COUPLING CONSTANT 4 CONST = ABS(219.8 * AH**2 + 13.17 * AC**2 + 107.7 * AH * AC + 1 3.997 * AH * ACP + C.973 * AC * ACP - 2.75*ACP**2) 5 RETURN END

1.) 1

1

-1.16-

\$IBFTC HOLAG SUBROUTINE HDIAG (H,N,IEGEN,U,NR) MIHDIS, FORTRAN II. DIAGONALIZATION OF A REAL SYMMETRIC MATRIX BY . 0010 0020 С С THE JACOBI METHOD. 0036 0046 MAY 19, 1959 C С CALLING SEQUENCE FOR DIAGENALIZATION 6050 CALL HUIAG(H, N, IEGEN, U, NR) WHERE H IS THE ARRAY TO BE DIAGONALIZED. C 0660 С C07C. Ċ N IS THE ORDER OF THE MATRIX, H. 0080 ۵ 0090 TEGEN MUST BE SET UNEQUAL TO ZERO IF UNLY DIGENVALUES ARE С 0100 Ĉ TO BE COMPLIED. 6116 С TEGEN MUST BE SET EQUAL TO ZERG IF EIGENVALUES AND EIGENVECTORS 0120 c C ARE TO BE COMPUTED. 0136 - 0140 С U IS THE UNITARY MATRIX USED FOR FORMATION OF THE EIGENVELTORS. 0150 С 0160 С NR IS THE NUMBER OF ROTATIONS. 0170 С 6180 - A DIMENSION STATEMENT MUST BE INSERTED IN THE SUBROUTINE. С 0190 С DIMENSION H(N,N), U(N,N), X(N), IQ(N) 0200 С 0210 THE SUBROUTINE OPTRATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE С 0220 RIGHT OF THE MAIN DIAGONAL. THUS, DALY A TRIANGULAR SECTION NEED BE STORED IN THE ARRAY H. Ċ 6236 С 0240 С 0256 C 0260 С 6270 С 0280 DIMENSION H(41,41), U(41,+1), X(41), IQ(41) IF (N- 1) 1000, 1000, 9 0310 9 IF (IEGEN) 15, 10, 15 0320 10 00 14 I=1,N 6330 00 14 J=1,N 0340 IF(I-J)12,11,12 0350 11 U(I,J)=1.() C360 GU TO 14 C37C 12 U(I,J)=C.U. 0380 14 CONTI NUE 0390 С 0400 15 $N\bar{R} = 0$ 0410 6 6420 С. SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW 0430 С X(I) CONTAINS LARGEST ELEMENT IN ITH ROW 0440 0440 - C450 C. IG(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT C 0460 17 NM[1=K-1 0470 DO 30 I=1,NMI1 0480 . C49Ű X(I) = 0.0IPL1=1+1 0506 DO 30 J=19L1;N 051Ŭ IF (x(1) - ABS(0(1,J))) 20,20,30 0520 20 X(I) = BS(H(I,J))0530 1Q(I)-J 0540 30 CONTINUE 0550 6560

C

	SET INDICATOR FOR SHE					
		UT-CEF_RAP=2	**-2/*****	O. CF ROL	AF10MS	
	0.50- 7450586596-02	-,				
		1997 - C. 1997 -				
	HU1E31=1-0000	·				
	The Automa OF 111	6 501 011 CT	CLOWENT .			
í	FIND MAXIMUM UP X(1)	S FUR PIVUL	CLEMENT /			
	TEST FOR END OF PRUSI	LC M			· · · · ·	
					•	
	DC 73 I=L,NMI1			,		
	IF (I-1) 60,60,45					
	TE (XMAX- X(1)) 20.	70.70				
			•	•		
		•				
			,			· ·
	CUNITIOE			· .		
						•
	IS MAX. X(I) EQUAL (O ZERO, IF L	ESS THAN I	JULESI, KE	AIRE HUIER	i
	IF (XMAX) 1000,1000	.86				
	IF (HUTESY) 90,90,85			· · ·	· • ·	
	IF $(XMAX - HDTEST)$ 9	0.90.148				
	HOIMIN = ARSE HILLIN)				
	-102024 = 00000000000000000000000000000000	•				
		(111 313 11	0 : 100			
	15 THEIMIN- ADST HTT	9/1/11 IIU+II	OF THO ?			
	HCIMIM=ABS(H(I,I))				•	
	CONTINUE					
	HOTESI=HDIMIN*RAP					
				`		
	RETURN DE MAX.H(I.J)	LESS THAN (2+	*-27) AUSE	(II(K,K)-HI)	v }	
	$T_{r}^{r} = \{ A_{r} \in T_{r} \in S_{r}^{r} = \{ A_{r} \in S_{r}^{r} \} $	2 1000 1000 1000			· ·	
	NO - ADIA	01100011000				
	NK = GR + I					
	COMPUTE TANGENT, JIN	e and custar	10111111			
	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT)	V, INIA)-H(Jb	IA ¹ Dili	≉H(IPIV,J	PIV)/(AES(H(IPI
	COMPULE TANGENT, JIN TANG=SIGN(2.0,(H(LPL IV,IPIV)-H(JPLV,JPLV)	V, IPIV)-H(JP)+SQRT((H(IP	IV,JP[V]) 1V,[P[V])-H	-(15IA*16[A*1) ≉H(I5IA*1) 2421	PIV)/(ACS(V))##2+4=0	⊢(IPI ∗Н(IP
	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT IV, IPIV)-H(JPIV, JPIV) 2IV, JPIV)++2))	2 ARB CCSIRC V, [PIV)-H(JP)+SQRT((H(IP	1V,JP[V]) 1V,[P[V]-	-(JPIV,JPI)	PIV)/(ACS(/))##2+4.0	н(191 *Н(19
	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPT IV,IPIV)-H(JPIV,JPIV) 2IV,JPIV)##2)) COSINE=1.0/SGRT(1-0+)	V, IPIV)-H(JP)+SQRT((H(IP TANG**2)	+H(1,1),H IV,JP[V}) IV,[P[V}−!	-(161A*) -(161A*) -(161A*)	PIV)/(AES(V))##2+4=0	⊢(IPI ∗Н(IP
	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPT IV,IPIV)-H(JPIV,JPIV) 2IV,JPIV)**2)) COSINE=1.C/SORT(1.0+ SINE=TAMUSECSINE	TANG**2)	IV,JP[V]) 1V,[P[V]-		PIV}/(ACS(V}}##2+4.0	н(IРI ∗н(IР
	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(TPT LV,TPTV)-H(JPTV,JPTV) 2TV,JPTV)++2)) COSINE=1.G/SGRT(1.0+ SINE=TANU*COSINE	V, IPIV)-H(JP)+SQRF((H(IP TANG**2)	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	-{V141} 14C+V14C}	×IV)/(AES(V))**2+4.0	н(IРI ≠н(IР
1	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPI V,IPIV)-H(JPIV,JPIV) 21V,JPIV)**2)) COSINE=1.C/SQRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,1PIV)	V, IPIV)-H(JP)+SQRF((H(IP TANG**2)		940(IPIV,J 7(JPIV,JPI	PIV)/(AES(V))**2+4.0	H(IPI +H(IP
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(TPT V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=1.G/SQRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE*	*2*(H11+TANG	+(2.0+F(1)	>IA'A5IA'A5IA'+	PIV)/(AES(V))**2+4.0 TANG*H(JPI	H(IPI ★H(IP V,JPI
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPI V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=1.G/SQRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE* V)))	*2*(H11+TANG	+((,1), IV,JP[V]) IV,[P[V]-! +(2.0+F(])	>IA ¹ 01A1A1A1 +(151A ⁺ 01A1A1)+	PIV)/(AES(V))**2+4.0 TANG*H(JPI	H(IP] ★H(IF V,JP]
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(TPT V,IPIV)-H(JPIV,JPIV) TV,JPIV)**2)) COSINE=1.G/SQRT(1.0+ SINE=TANG*COSINE HII=H(IPIV,IPIV) H(TPIV,[PIV)=COSINE** (JPIV,JPIV)=COSINE**	*2*(H(JPIV)-H(JP)+SQRT((H(IP TANG**2) *2*(H1I+TANG	+(2.C+F(1) PIV)-TANG	>IV,JPIV)+ *(2,0+H(IP)+ *(2,0+H(IP)	PIV)/(AES(V))##2+4=0 TANG#H(JPI [V,JPIV)-F	H(IP) *H(IF V,JP) ANG*H
12111	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPI V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=1.G/SQRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE* V))) H(JPIV,JPIV)=COSINE* II))	*2*(H(JPIV,J	+(2.0+F(1) PIV)-TANG	>!V,JP[V,JP] >!V,JP[V)+ !(2.5#H(IP	PIV)/(AES(V))##2+4=0 TANG#H(JPI IV,JPIV)-F	H(IPI *H(IP V,JPI ANG*H
1 2 1 1	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(TPT V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=1.G/SQRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,[PIV)=COSINE** I)) H(JPIV,JPIV)=COSINE** II)) H(IPIV,JPIV)=C.C	*2*(H(JPIV)-H(JP)+SQRF((H(IP TANG**2) *2*(H1I+TANG	+(2.0+F(1) PIV)-TANG	>H(IPIV,JPI (JPIV,JPI PIV,JPIV)+ (2.5*H(IP	PIV)/(AES(V))**2+4=0 TANG*H(JPI (V,JPIV)-f	H(IP] *H(IF V,JP] ANG*H
1 2 1 1 1	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT V, IPIV)-H(JPIV, JPIV) IV, JPIV)**2)) COSINE=1.G/SQRT(1.0+ SIME=TANG*COSINE HIT=H(IPIV, IPIV) H(IPIV, IPIV)=COSINE** I)) H(JPIV, JPIV)=COSINE** I)) H(IPIV, JPIV)=C.C	*2*(H(JPIV)-H(JP)+SQRF((H(IP TANG**2) *2*(H1I+TANG	+(2.0++(1) PIV)-TANG	>IV,JPIV,JPI <(2.5*H(IP)+ *(2.5*H(IP)	PIV)/(AES(V))**2+4=0 TANG*H(JPI IV,JPIV)-T	H (I P I * H (I F V → J P I ANG * H
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT V, IPIV)-H(JPIV, JPIV) IV, JPIV)**2)) COSINE=1.G/SGRT(1.0+ SINE=TANG*COSINE HIT=H(IPIV, IPIV) H(IPIV, JPIV)=COSINE** II)) H(JPIV, JPIV)=COSINE** II)) H(IPIV, JPIV)=C.C	*2*(H(JPIV)-H(JP)+SQRT((H(IP TANG**2) *2*(H1I+TANG *2*(H(JPIV,J	+(2.C+F(1) +(2.C+F(1) PIV)-TANG	YIQI 90, VIQI 190, VIQU 190, VIQU 190, VIQU +(VIQU +(VIQU +(VIQU +(VIQU) +(VI	PIV)/(AES(V))**2+4.0 TANG*H(JPI [V,JPIV)-f	H(IPI *H(IP V,JPI ANG*H
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(TPT V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=1.G/SQRT(1.0+ SINE=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE* V))) H(JPIV,JPIV)=COSINE* II)) H(IPIV,JPIV)=C.C PSEUDO RANK THE EIG	<pre>P + SQR F (H (I P + SQR F ((H (I P T A NG * * 2) * 2 * (H I I + T A NG * 2 * (H (J P I V + J ENVALUES E (D = C P (D + T + T)</pre>	+(2.0++(1) PIV)-TANG	>+H(IPIV,J (JPIV,JPI >(JPIV,JPI)+ +(2.5+H(IP	PIV)/(AES(y))##2+4=0 TANG#H(JPI IV,JPIV)-F	н(191 *н(19 v,јр] Ang*f
	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT V, IPIV) = H(JPIV, JPIV) IV, JPIV) **2)) COSINE=1.G/SQRT(1.0+ SINE=TANG*COSINE HII=H(IPIV, IPIV) H(IPIV, IPIV)=COSINE* V)) H(JPIV, JPIV)=COSINE* II)) H(IPIV, JPIV)=0.C PSEUDO RANK THE EIGH ADJUST SINE AND COS	<pre>PART (PIV)-H(JP)+SQRT((H(IP TANG**2) *2*(H1I+TANG *2*(H(JPIV,J ENVALUES FOR COMPUTA</pre>	+(2.0+F(1) PIV)-TANG	<pre>>*H(IPIV,J (JPIV,JPI >IV,JPIV)+ *(2.5*H(IP (IK)_AND_U</pre>	PIV)/(AES(V))##2+4=0 TANG#H(JPI [V,JPIV)-F (1K)	н(ІР) *н(ІР v,јр] ang*f
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPT V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=1.G/SGRT(1.0+ SINE=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE* V))) H(JPIV,JPIV)=COSINE* II)) H(IPIV,JPIV)=C.C PSEUDO RANK THE EIG ADJUST SINE AND COS IF (m(IPIV,IPIV) -	<pre>Find Control () () () () () () () () () () () () () () (</pre>	+(2.0++(1) +(2.0++(1) PIV)-TANG TION OF H)) 152,15	<pre>>+H(IPIV,J (JPIV,JPI >IV,JPIV)+ +(2.5+H(IP (IK) AND U 3,153</pre>	PIV)/(AES(V))**2+4=0 TANG*H(JPI (V,JPIV)-T (IK)	Η (1 Ρ] *Η (1 F V → J Ρ] ANG * H
1	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT LV, IPTV) - H(JPTV, JPTV) 21V, JPTV) + + (JPTV, JPTV) 21V, JPTV) + + 2)) COSINE=1. G/SGRT(1.0+ SIME=TANG*COSINE HIT=H(IPTV, IPTV) = COSINE+ H(IPTV, JPTV) = COSINE+ LIT)) H(JPTV, JPTV) = COSINE+ LIT)) H(IPTV, JPTV) = COSINE+ ADJUST SINE ANC COS IF (::(IPTV, IPTV) - HTEMP = H(IPTV, IPTV)	<pre>v, IPIv)-H(JP v, IPIv)-H(JP tANG**2) *2*(H(I+TANG *2*(H(JPIv,J ENVALUES FOR COMPUTA H(JPIV,JPIV</pre>	+(2.0++(1) +(2.0++(1) PIV)-TANG TIUN OF H)) 152.15	(IK) AND U (J) AND U (IK) AND U (IK) AND U (IK) AND U	PIV)/(AES(V))**2+4=0 TANG*H(JPI [V,JPIV)-F (IK)	H(IP) *H(IF V,JP) ANG*H
	CGMPUIE TANGENT, JIN TANG=SIGN(2.0,(H(IPI IV,IPIV)-H(JPIV,JPIV) 2IV,JPIV)*2)) COSINE=1.G/SQRT(1.0+ SINE=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE* IV))) H(JPIV,JPIV)=COSINE* II)) H(IPIV,JPIV)=COC PSEUDD RANK THE EIG ADJUST SINE AND COS IF (h(IPIV,IPIV) - HIEMP = H(IPIV,IPIV) H(IPIV,IPIV) = H(JPIV)	<pre>v, IPIv)-H(JP v, IPIv)-H(JP tang**2) *2*(H1I+TANG *2*(H(JPIv,J ENVALUES FOR COMPUTA H(JPIV,JPIV v, JPIV)</pre>	+(2.0+F(1) +(2.0+F(1) PIV)-TANG TION OF H) 152,15)*H(IPIV,J (JPIV,JPI PIV,JPIV)+ *(2.0*H(IP (IK) AND U 3,153	PIV)/(AES(y))##2+4=0 TANG#H(JPI [V,JPIV)-f (1K)	н(ІРІ *н(ІР v,јрі Ang*н
122	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT LV, IPTV)-H(JPTV, JPTV) 21V, JPTV)**2)) COSINE=1.G/SQRT(1.0+ SINE=TANG*COSINE HIT=H(IPTV, IPTV) H(IPTV, JPTV)=COSINE** II)) H(IPTV, JPTV)=COSINE** II)) H(IPTV, JPTV)=COSINE** ADJUST SINE AND COS IF (H(IPTV, IPTV) - HTEMP = H(IPTV, IPTV) H(IPTV, JPTV) = H(JPTV) H(IPTV, JPTV) = H(JPTV)	<pre>v, IPIv)-H(JP v, IPIv)-H(JP rang**2) *2*(H1I+TANG *2*(H(JPIv,J ENVALUES FOR COMPUTA H(JPIV,JPIV) v, JPIV)</pre>	+(2.0++(1) +(2.0++(1) PIV)-TANG TICN OF H)) 152+15	<pre>>+H(IPIV,J (JPIV,JPI >IV,JPIV)+ +(2.5+H(IP (IK) AND U 3,153</pre>	PIV)/(AES(V))**2+4=0 TANG*H(JPI [V,JPIV)-F (IK)	H(IPI ★H(IP V,JPI ANG*H
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(TPT V,IPIV)-H(JPIV,JPIV) PIV,JPIV)**2)) COSINE=I.G/SGRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,JPIV)=COSINC*(V))) H(JPIV,JPIV)=COSINE*(II)) H(IPIV,JPIV)=0.C PSEUGO RANK THE TIGH ADJUST SINE ANC COS IF (::(IPIV,IPIV) - HIEMP = H(IPIV,IPIV) H(JPIV,JPIV) = H(JPI) H(JPIV,JPIV) = H(JPI)	<pre>v, IPIv)-H(JP)+SQRT((H(IP TANG*+2) *2*(H1I+TANG *2*(H(JPIv,J ENVALUES FOR COMPUTA H(JPIV,JPIV v,JPIV) COS</pre>	+(2.0++(1) +(2.0++(1) PIV)-TANG TICN OF H)) 152,15	(IK) AND U (3,153)	PIV)/(AES(V))**2+4.0 TANG*H(JPI (V,JPIV)-F (IK)	H(IPI *H(IP V,JPI ANG*H
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(TPT LV, IPTV)-H(JPTV, JPTV) 21V, JPTV)++(JPTV, JPTV) 21V, JPTV)++2)) COSINE=1.G/SGRT(1.0+ SIME=TANG*COSINE HIT=H(IPTV, IPTV) H(IPTV, IPTV)=COSINE++ IT)) H(JPTV, JPTV)=COSINE++ IT)) H(IPTV, JPTV)=0.C PSEUDO RANK THE EIGN ADJUST SINE AND COS IF (H(IPTV, IPTV)- HTEMP = H(IPTV, IPTV)- H(IPTV, JPTV) = H(JPTV) H(JPTV, JPTV) = H(JPTV)- H(JPTV, JPTV) = HTMP RECOMPUTE SINE AND	<pre>Find control () () () () ()) + SQRT(() () TANG**2) *2*() () () () *2*() () () () *2*() () *2*()) *2*() () *2*() () *2*())) *2*())) *2*())) *2*()</pre>	+(2.0++(1) +(2.0++(1) PIV)-TANG TIUN OF H)) 152.15	<pre>>*H(IPIV,J (JPIV,JPI >IV,JPIV)+ *(2.0*H(IP (IK) AND U 3,153</pre>	PIV)/(AES(V))**2+4=0 TANG*H(JPI [V,JPIV)-F (IK)	H(IPI ★H(IP V,JPI ANG*H
1	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPI IV,IPIV)-H(JPIV,JPIV) 2IV,JPIV)*2)) COSINE=1.G/SQRT(1.0+ SINE=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE* IV))) H(JPIV,JPIV)=COSINE* II)) H(IPIV,JPIV)=COSINE* II)) H(IPIV,JPIV)=COSINE* II)) H(IPIV,JPIV)=COSINE* IF(:(IPIV,IPIV)= HIEMP = H(IPIV,IPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV,JPIV) = H(JPIV)	V, IPIV)-H(JP V, IPIV)-H(JP I+SQRF((H(IP TANG**2) *2*(H1I+TANG *2*(H(JPIV,J ENVALUES FOR COMPUTA H(JPIV,JPIV V,JPIV) CDS INF) * COSIN	+(2.0++(1) +(2.0++(1) PIV)-TANG TIUN OF H)) 152,15)*H(IPIV,J (JPIV,JPI (JPIV,JPI *(2.0*H(IP (IK) ΔND U 3,153	PIV)/(AES(y))##2+4=0 TANG#H(JPI [V,JPIV)-f (IK)	H(IPI ★H(IP V,JPI ANG*H
12	COMPUTE TANGENT, JIN TANG=SIGN(2.0,(H(IPT V,IPIV)-H(JPIV,JPIV) IV,JPIV)**2)) COSINE=I.G/SGRT(1.0+ SIME=TANG*COSINE HII=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE*(V))) H(JPIV,JPIV)=COSINE*(II)) H(IPIV,JPIV)=COSINE*(ADJUST SINE AND COS IF (H(IPIV,IPIV)- HIEMP = H(IPIV,IPIV)- H(JPIV,IPIV) = H(JPIV) H(JPIV,IPIV) = H(JPIV) H(JPIV,IPIV) = H(JPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV) H(JPIV,JPIV) = H(JPIV) H(JPIV) = H(JPIV)	V, IPIV)-H(JP V, IPIV)-H(JP TANG**2) *2*(H1I+TANG *2*(H(JPIV,J ENVALUES FOR COMPUTA H(JPIV,JPIV V,JPIV) CDS INF) * COSIN	+(2.0++(1) +(2.0++(1) PIV)-TANG TICN OF H)) 152,15)*H(IP[V,J (JPIV,JPI >IV,JPIV)+ *(2.5*H(IP (IK) AND U 3,153	PIV)/(AES(V))**2+4=0 TANG*H(JPI (V,JPIV)-T (IK)	H(IPI *H(IP V,JPI ANG*H
	COMPUTE TANGENT, JIN TANG=SIGN(2.0, (H(IPT /,IPIV)-H(JPIV,JPIV) IV,JPIV)+*2)) COSINE=1.G/SGRT(1.0+ SINE=TANG*COSINE HI=H(IPIV,IPIV) H(IPIV,IPIV)=COSINE++ II)) H(JPIV,JPIV)=COSINE++ II)) H(IPIV,JPIV)=COSINE++ II)) H(IPIV,JPIV)=COSINE++ ADJUST SINE AND COS IF (SI(IPIV,IPIV)- H(IPIV,IPIV)=H(JPI) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPI) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(IPIV,IPIV)=H(JPIV) H(JPIV,IPIV)=H(JPIV) H(JPIV,IPIV)=H(JPIV) H(JPIV,IPIV)=H(JPIV) H(JPIV)=H(JPIV) H(JPIV)=H(JPIV) H(JPIV)=H(JPIV) H(JPIV)=H(JPIV)	<pre>V, IPIV)-H(JP V, IPIV)-H(JP TANG*+2) *2*(H(I+TANG *2*(H(JPIV,J ENVALUES FOR COMPUTA H(JPIV,JPIV V,JPIV) CDS INF) * COSIN</pre>	+(2.0++(1) +(2.0++(1) PIV)-TANG TICN OF H)) 152,15	<pre>>*H(IPIV,J (JPIV,JPI) >IV,JPIV)+ *(2.0*H(IP (IK) AND U 3,153</pre>	PIV)/(AES(V))**2+4.0 TANG*H(JPI (V,JPIV)-f (IK)	H(IPI *H(IP V,JPI ANG*H

INSPECT THE IGS BETWEEN I+1 AND N+1 TO DETERMINE WHETHER A NEW MAXIMUM VALUE SHOULD BE COMPUTED SINCE THE PRESENT MAXIMUM IS IN THE 1 OR J RCW. DO 350 1=1;NMI1 IF(I-1PIV)210,350,200 200 IF(I-JPIV)210,350,210 IF(IQ(I)-IPIV)230,240,230 IF(IQ(I)-JPIV)350,240,350 κ=iq(1) HIEMP=H(L,K) H(I,K) = 0.01PL1=1+1 X(I) =0.0

SEARCH IN DEPLETED ROW FOR NEW MAXIMUN

00 320 J=1PL1.N IF (X(I)- ABS(H(I,J))) 300,300,320 -x(I) = ABS(H(I,J))300 IQ(I) = J320 CONTINUE

H(I,K)=HTEMP 350 CONTINUE

C.

С

С

Ċ

210

230

240

250

С

£

С

Ċ

6

С

С

С

C

X(IPIV) = 0.0X(JPIV) = 0.C

CHANGE THE OTHER CLEMENTS OF H

00 530 1=1.N

IF(I-(PIV)370,530,420 370 HIENP = H(I, IPIV)H(I, IPIV) = CUSIGI+HTEMP + SINE+H(I, JPIV) IF (x(1) - A2S(H(I, IPIV)))380,390,390 X(I) = ABS(H(I, IPIV))38C IC(I) = IPIVH(I, JPIV) = -SINE = H(EMP + CCSINE = H(I, JPIV)IF (X(I) - ABS(H(I, JPIV))) 400,530,530 390 400 X(I) = ABS(H(I, JPIV))V19U = (1)01

GO TU 530

420 - IF(I-JPIV)430,530,480 430 HIEMP = H(IPIV, I)H(IPIV,I) = COSINC *HTEMP + SINE*H(1,JPIV) IF (X(IPIV) - APS(H(IPIV,I))) 440,450,480 X(IPIV) = ABS(H(IPIV,I))44(. IQ(IPIV) = IH(I, JPIV) = -SINE®HTEMP + COSINE®H(I, JPIV) 45Ŭ IF (X(I) - ABS(H(I, JPIV))) 400,530,530

480 = HTEMP = H(IPIV,I)H(IPIV,I) = COSINC+HTEMP + SINE+H(JPIV,I) IF (X(IPIV) - "ABS(H(IPIV,I))) 490,500,500

1130

1140

1150

1160

117Ù

1130 1190

1200

1210

1220

1230

1240

1250

1260

1270

1280

1290

1300

1310

1320

1330

1340

1350 1360

1370

1380

1390

1400

1410

1426

1430

1440

145C

1460

1470

1480

1490

1500

1510

1520 1530

1546 1550

1560

1570

1580

1590

1600 1610

1686

С

•

490	X(IPIV) = ABS(H(IPIV,I))
	IC(IPIV) = I
500	H(JPIJ,1) = -SINE*HIEMP + COSINE*H(JPIV.1)
	IF (A(JPIV) - AUS(H(JPIV.[))) 510.530.530
510.	X(JPIV) = ABS(H(JPIV, I))
	IQ(JP(V) = I
530	CONTINUE
C	
C .	TEST FOR COMPUTATION OF EIGENVECTORS
C	
	IF(IESEN)40,540,40
540	DO 550 1=1.N
	HTEMP=U(1, IPIV)
	U(I,LPIV)=COSINE+HTEMP+SINE+U(I,JPIV)
550	U(1, JPIV) =- SINE #HIEMP+CCSINE *U(1, JPIV)
	SU TO 40
1000	NC = N - 1
	DO 1001 I = 1.NO
	VST = I + I
	DC 1001 J = NST, V
1001	H(J,I) = H(I,J)
	RETURN
	END

7

•

•

• •

, ,

APPENDIX III

CALCULATIONS ON RADICAL CATIONS

									······································		
			•	•		i.					
Radical Cation		1	2	3	4	5	6	7	8	9	10
2,3 dimethyl butadier	L 1e	59484	33853	.08374	.15666					-	
Isoprene		.62503	•36928	09430	17290	33518	56731				
l,3 cyclo- hexadiene		35303	51963	.14187	.29194			•			
Toluene ¹	a b	0 • 5286 5	5000 .23764	5000 31500	0 52084	0 .21281	0 •30423		·		
an a				ч.					·		
	a	28999	56546	24715	.10992	•15162					
o-xylene	Ъ	.41703	06327	47070	.17723	.26290					
	a	0	.48830	.42189	0	16288	23883				
m-xylene	b	51267	24151	.28513	.60526	12515	17356				
p-xylene ²	b a	50000 .27218	0 •49607	0 17937	0 27125				·		
Acenapthene		Ο ·	.40673	.21864	28914	37416	0	•11573	.22306		
Pyracene		.24963	•36743	0	10031	28643				- -	
9 methyl anthracene		44987	08705	• 30418	.20476	22494	- 29181	.11201	.42220	07977	17986
9,10 dimeth; anthracen	yl e	21008	28564	.10734	•43159	07822	18198				

Table XXI. Huckel Molecular Orbital Coefficients Neglecting Overlap for Radical Cations

See Fig. 12 for numbering

a Antisymmetric orbital

b Symmetric orbital

-155-

						·				
ρ _i			• • • •		i					
Radical Cation	1	2	3	14	5	6	7	8	9	10
2,3 dimethyl butadiene	•43407	.07868	01449	.00174						
Isoprene	•44555	.11289	01800	.00416	.06006	•3953 ⁴				1
1,3 cyclo- hexadiene	.11043	•35451	02037	.05542						•
Toluene b c	03704 .62725	.27314 17014	.26970 07484	00988 .58898	01882 .07809	01994 .19564				
b	•06983	•39687	.07006	02623	01052					
o-xylene c	.27468	33664	.407.98	.03728	.11670					
m-xylene c	98475 .35716	.47061 .04903	.26783 .08879	-•39368 •43637	.02329 02721	•07749 -•00738				
p-xylene c b	.27263 .05564	01966 00215	01151 .31373	01409 .06639						
Acenapthene	03566	.20813	•03333	.08281	.17130	02691	00462	.04035		
Pyracene	.05874	.16852	02771	00309	.03968					
9 methyl anthracene	.27247	01977	.10014	.03112	.04155	.08914	00820	.23077	00485	.03366
9,10 dimethyl anthracene	.03572	.08774	00994	.24281	00509	.03523				
a) Ref 69	$\lambda = 1.00$	• b) Ant	iarmotria	ombitol.		hand a control due	. 1			

Table XXII. McLachlan^a SCF Spin Densities for Radical Cations

Antisymmetric orbital; c) Symmetric orbital. a)

See Fig. 12 for numbering.

-123-

C _i						i					
Radical Cation		. 1	2	3	4	5	6	·7	8	9	10
2,3 dimethy butadie	1 ne	55488	31372	.08391	•14773						i.
Isoprene		.58433	•34384	09540	16420	30950	52596				
1,3 cyclo- hexadiene		32988	48209	•14135	•27740						
Toluene	a b	0 47004	44721 20854	44721 .28499	0 .46143	0 21123	0 281 <i>9</i> 6				
				<i>,</i>					•		
	a	25988	50512	21677	.11025	.14121					
o -xylene	b	36876	.06191	.42028	17431	24276			•		
m-xylene	a b	0 .45080	.43890 .21051	•37324 25420	0 - • 54436	15987 .12691	21950 .16369	-			
p-xylene	a b	.44721 24464	0 44184	0 •17517	0 .24902						
Acenapthene	e	· 0	•37835	.20073	27185	34496	Ö	.11689	•21313		
Pyracene		.23326	.34089	0	09995	19615					
9 methyl anthracene		42953	08276	.28968	•19439	21477	27715	.10796	.40152	08052	.17251
9,10 dimeth	nyl ne	.20014	.27150	10332	41167	.07874	.17476		·		

Table XXIII. Huckel Molecular Orbital Coefficients Including Overlap for Radical Cations

^aAntisymmetric orbital

^bSymmetric orbital

-124-

REFERENCES

l.	C. A. Coulson, Rev. Mod. Phys. <u>32</u> , 169 (1960).
2.	M. H. L. Pryce, Proc. Phys. Soc. <u>A63</u> , 25 (1950).
3.	A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. <u>205A</u> , 135 (1951).
4.	B. Bleaney and K. W. H. Stevens, Rep. Prog. Phys. <u>16</u> , 108 (1953).
5.	G. E. Pake, Paramagnetic Resonance, (Benjamin, New York, 1962) Chap. 3
6.	A. J. Stone, Proc. Roy. Soc. <u>271A</u> , 424 (1963).
7.	H. A. Jahn and E. Teller, Proc. Roy. Soc. <u>A161</u> , 220 (1937).
8.	A. J. Stone, Mol. Phys. <u>6</u> , 509 (1963).
9.	D. E. Ingram, Free Radicals as Studied by Electron Spin Resonance,
	(Butterworth Scientific Publications, London, 1958).
10.	S. I. Weissman, J. Chem. Phys. <u>22</u> , 1378 (1954).
11.	E. Fermi, Z. Physik <u>60</u> , 320 (1930).
12.	R. G. Parr, <u>Quantum Theory of Molecular Electronic Structure</u> , (W. A.
	Benjamin, Inc., New York, 1963) p. 42.
13.	H. M. McConnell, J. Chem. Phys. <u>24</u> , 632, 764 (1956).
14.	H. M. McConnell and H. H. Dearman, J. Chem. Phys. <u>28</u> , 51 (1958).
15.	H. M. McConnell and D. B. Chesnut, J. Chem. Phys. <u>28</u> , 107 (1958).
16.	J. P. Colpa and J. R. Bolton, Mol. Phys. <u>6</u> , 273 (1963).
17.	G. Giacometti, P. L. Nardio and M. V. Pavan, Theoret. Chim. Acta. 1,
	404 (1963).
18.	A. D. McLachlan, H. H. Dearman, and A. Lefebvre, J. Chem. Phys., <u>33</u> ,
	65 (1960).
19.	M. Karplus and G. K. Fraenkel, J. Chem. Phys., <u>35</u> , 1312 (1961).
20.	S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, J. Chem.

-125-

Phys., <u>21</u>, 2227 (1953).

21.	T. L. Chu	G. E.	Pake, D.	E. Paul,	J. Townsend,	and S. I.	Weissman,
	J. Phys.	Chem.,	<u>57</u> , 504	(1953).			

- 22. D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, Science, <u>117</u>, 534 (1953).
- 23. G. K. Fraenkel and B. Segal, Ann. Rev. Phys. Chem. 10, 435 (1959).
- 24. R. Bersohn, <u>ibid</u>. <u>11</u>, 369 (1960).
- 25. S. I. Weissman, <u>ibid</u>. <u>12</u>, 151 (1961).
- 26. A. G. Shulman, <u>ibid</u>. <u>13</u>, 325 (1962).
- 27. D. Kivelson and C. Thomson, <u>ibid</u>. <u>15</u>, 197 (1964).
- 28. S. A. Al'tshuler and B. N. Kozyrev, <u>Electron Paramagnetic Resonance</u>, (Academic Press, New York, 1964).
- 29. A. Carrington, Quart. Rev. <u>17</u>, 67 (1963).
- 30. D. E. Paul, D. Lipkin, S. I. Weissman, J. Am. Chem. Soc. 78, 116 (1956).
- 31. T. R. Tuttle and S. I. Weissman, ibid. 80, 5342 (1958).
- 32. H. W. Bowers and F. D. Greene, J. Am. Chem. Soc. 85, 2331 (1963).
- 33. D. H. Geske and A. H. Maki, J. Am. Chem. Soc., <u>82</u>, 2671 (1960))
- 34. P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, J. Am. Chem. Soc. <u>85</u>, 683 (1963).
- 35. E. W. Stone and A. H. Maki, J. Chem. Phys. <u>39</u>, 1635 (1963).
- 36. L. H. Piette, P. Ludwig and R. N. Adams, J. Am. Chem. Soc. <u>84</u>, 4212 (1962).
- 37. L. H. Piette, P. Ludwig and R. N. Adams, J. Am. Chem. Soc. <u>83</u>, 3909 (1961).
- 38. C. A. Kraus, J. Chem. Ed. <u>30</u>, 83 (1953).
- 39. W. L. Jolly, Progress. Inorg. Chem. 1, 235 (1959).
- 40. M. C. R. Symons, Quart. Rev. <u>13</u>, 99 (1959).
- 41. G. Lepoutre and M. J. Sienko, <u>Solutions Metal-Ammoniac</u>: <u>Proprietes</u> <u>Physics-Chimiques</u>, (W. A. Benjamin, New York, 1964).

- 42. C. A. Kraus, J. Am. Chem. Soc. <u>30</u>, 1323 (1908).
- 43. S. Freed and N. Sugarman, J. Chem. Phys. <u>11</u>, 354 (1943).
- 44. R. A. Ogg, Phys. Rev. <u>69</u>, 668 (1946).
- 45. R. A. Ogg, J. Chem. Phys. 14, 114 (1946).
- 46. E. Becker, R. H. Lindquist, B. J. Alder, J. Chem. Phys. 25, 971 (1956).
- 47. H. M. McConnell and C. H. Holm, J. Chem. Phys. <u>26</u>, 1517 (1957).
- 48. J. V. Acrivos and K. S. Pitzer, J. Phys. Chem. <u>66</u>, 1693 (1962).
- 49. M. Gold, W. L. Jolly and K. S. Pitzer, J. Am. Chem. Soc. <u>84</u>, 2264 (1962).
- 50. H. A. Laitinen and C. H. Nyman, J. Am. Chem. Soc. <u>70</u>, 3002 (1948).
- 51. G. S. Forbes and C. E. Norton, J. Am. Chem. Soc. <u>48</u>, 2278 (1926).
- 52. L. R. Doyle, "The ESR Absorption of Two Solid-State Paramagnetic Centers", Lawrence Radiation Laboratory Report, UCRL-9602, March 1961.
- 53. A. J. Birch and H. Smith, Quart. Rev. <u>12</u>, 17 (1958).
- 54. H. Smith, <u>Chemistry in Non-Aqueous Ionizing Solvents</u>, Part I, Vol. 2, (Interscience Publishers, New York, 1963).
- 55. N. Edelstein, "A Study of the Kinetics of the Reaction H + 0₂ by Paramagnetic Resonance", Lawrence Radiation Laboratory Report, UCRL-10108, April 1962.
- 56. F. R. Jensen and L. A. Smith, J. Am. Chem. Soc. <u>86</u>, 956 (1964).
- 57. R. G. Parr and R. S. Mulliken, J. Chem. Phys. 18, 1338 (1950).
- 58. C. Sandorfy, <u>Electronic Spectra and Quantum Chemistry</u>, (Prentice-Hall Publishing Company, Inc., Englewood Cliffs, New Jersey, 1964).
- 59. H. L. Strauss, T. J. Katz, and G. K. Fraenkel, J. Am. Chem. Soc. <u>85</u>, 2360 (1963).
- 60. A. Streitweiser, <u>Molecular Orbital Theory</u>, (John Wiley and Sons, Inc., New York, 1961).

- 61. O. Sovers and W. Kauzmann, J. Chem. Phys. <u>38</u>, 813 (1963); O. Sovers, Thesis, Princeton University, 1961.
- 62. R. Hayes, Private communication.
- 63. J. R. Bolton, A. Carrington, and A. D. McLachlan, Mol. Phys. <u>5</u>, 31 (1962).
- 64. J. P. Colpa and E. DeBoer, Mol. Phys. 7, 333 (1964).
- 65. R. S. Mulliken, C. H. Rieke and W. G. Brown, J. Am. Chem. Soc. <u>63</u>,
 41 (1941).
- 66. C. A. Coulson and V. A. Crawford, J. Chem. Soc. <u>1953</u>, 2052.
- 67. P. Lowdin, J. Chem. Phys. <u>18</u>, 365 (1950).
- 68. G. Goertzel and N. Tralli, <u>Some Mathematical Methods of Physics</u>, (McGraw-Hill, New York, 1960) Chapter 2.
- 69. A. D. McLachlan, Mol. Phys. <u>3</u>, 233 (1960).
- 70. R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. <u>17</u>, 1248 (1949).
- 71. D. G. Chesnut, J. Chem. Phys. 29, 43 (1958).
- 72. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. <u>39</u>, 2147 (1963).
- 73. R. J. Myers, unpublished results.
- 74. J. R. Bolton, J. Chem. Phys. <u>41</u>, 2455 (1964).
- 75. J. R. Bolton and A. Carrington, J. Chem. Phys. <u>4</u>, 497 (1961).
- 76. A. D. McLachlan, Mol. Phys. 2, 271 (1959).
- 77. E. DeBoer and S. I. Weissman, J. Am. Chem. Soc. 80, 4549 (1958).
- 78. M. C. R. Symons, J. Chem. Soc. <u>48</u>, 277 (1959).
- 79. C. Hellerland H. M. McConnell, J. Chem. Phys. <u>32</u>, 1535 (1960).
- 80. E. W. Stone and A. H. Maki, J. Chem. Phys. <u>37</u>, 1326 (1962).
- 81. P. H. Rieger and G. A. Fraenkel, J. Chem. Phys. <u>39</u>, 609 (1963).
- 82. P. Ludwig, T. Layloff and R. N. Adams, J. Am. Chem. Soc. 86, 4568 (1964).

E.

83.	T.	J.	Katz	and	H.	L. Strauss,	J.	Chem.	Phys.	<u>32</u> ,	1873	(1960))	•
-----	----	----	------	-----	----	-------------	----	-------	-------	-------------	------	-------	----	---

- 84. E. W. Stone and A. H. Maki, J. Chem. Phys. <u>38</u>, 1999 (1963).
- 85. SHARE writeup J6 XYP2 MOD available from the Math and Computing Group, Lawrence Radiation Laboratory, Berkeley, California.
- 86. D. F. Stevens, "LRL 7040 IBSYS Users' Manual", University of California, Lawrence Radiation Laboratory, Berkeley, California. November 1964.
- 87. A. Almenninger, O. Bastiansen, and M. Traettenberg, Acta. Chem. Scand. <u>12</u>, 1221 (1958).
- R. G. Lawler, J. R. Bolton, G. K. Fraenkel and T. H. Brown, J. Am. Chem. Soc. <u>86</u>, 520 (1964).
- 89. H. L. Strauss, private communication.
- 90. R. W. Fessenden and S. Ogawa, J. Am. Chem. Soc. <u>86</u>, 3591 (1964).

91. M. T. Jones, J. Chem. Phys. <u>38</u>, 2892 (1963).

- 92. D. C. McCain, private communication.
- 93. T. H. Brown and M. Karplus, J. Chem. Phys. <u>39</u>, 1115 (1963).

94. P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. <u>37</u>, 2811 (1962).

FIGURE CAPTIONS

1.	Cell and Dewar for Electrolysis in Liquid Ammonia.
2.	Diagram of Cell and Dewar for Electrolysis in Liquid Ammonia.
3.	Experimental ESR Spectrum of 1,3-Butadiene.
4.	Calculated ESR Spectrum of 1,3-Butadiene.
5.	Bond Lengths and Angles of Methylene.
6.	Experimental ESR Spectrum of 2,3-Dimethyl Butadiene.
7.	Calculated ESR Spectrum of 2,3-Dimethyl Butadiene.
8.	Experimental ESR Spectrum of 1,3-Cyclohexadiene.
9.	Calculated ESR Spectrum of 1,3-Cyclohexadiene.
10.	Experimental ESR Spectrum of Isoprene. Arrows indicate anomolous lines.
11.	Calculated ESR Spectrum of Isoprene.
12.	Numbering System for Molecular Orbital Calculations.
13.	Experimental ESR Spectrum of 1,3,5-Cycloheptatriene.
14.	Calculated ESR Spectrum of 1,3,5-Cycloheptatriene.
15.	Numbering System for Cycloheptatriene.
16.	Experimental ESR Spectrum of Monodeuterated 1,3,5-Cycloheptatriene.
17.	Calculated ESR Spectra of the Four Possible Monodeuterated 1,3,5-Cyclo-
	heptatrienes.
18.	Experimental ESR Spectrum of Nitrosobenzene.
19.	Calculated ESR Spectrum of Nitrosobenzene.
20.	Numbering System for 2-Methylcyclohexadiene.

11

1.83

\$

. 5

ć

, ,

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.