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Abstract - That aspect of the NRCC's mission directed to advancing the capability of chemists to use computers has led to involvement in efforts to facilitate computations by theoretical chemists. The areas of greatest concentration include algorithm selection and software implementation. Experiences at the NRCC and their implications for the fields of collision dynamics, crystallography, graphics, macromolecular science, quantum chemistry, and statistical mechanics are briefly summarized. A recent study of the reaction of O with C_2H_4 is discussed to provide an illustration of progress in the understanding of reaction pathways using computational methods.

INTRODUCTION

The application of computers in theoretical chemistry is significantly extending both the qualitative and quantitative understanding of molecular processes. To describe the numerous advances made in recent years is beyond the scope of this paper and the interested reader is referred to appropriate journals and review periodicals. Rather the intent here is to provide insight into the areas of research activity that theoretical chemists who compute have focused on as reflected by experiences at the National Resource for Computation in Chemistry (NRCC).

ALGORITHMS AND SOFTWARE IMPLEMENTATION

Because of the availability of computers of different manufacture and machine precision, robustness, portability, and modularity have become the focus of increased attention by theoretical chemists. By robustness of a program, we mean the capability of a program to treat problems over widely varying parameter ranges without significant loss of accuracy or speed. Portability refers to the capability of running programs on different machines without the need for software changes. These areas, robustness and protability, coupled with modularity, were the subject of much discussion by quantum chemists and crystallographers at the NRCC's workshop on "Software Standards in Chemistry." The interested reader is referred to the proceedings of this meeting which contains a number of excellent articles addressing points discussed in this section (1).

Guidance in writing robust programs is usefully described at an elementary level by Forsythe, et al. (2) Two examples of robust software are the collections of FORTRAN subroutines called LINPACK (3) which solves simultaneous linear equations and EISPACK (4) which solves matrix eigenvalue problems. Tested mathematical software may also be purchased from, for example, IMSL (5) and NAG (6). It is important to bear in mind, however, that general purpose algorithms built for robustness by numerical analysts may not suffice for specific chemical applications because of repeated use which places a high premium on cost savings.

Portability is greatly aided for FORTRAN software by restriction to the PFORT subset of the 1966 ANSI FORTRAN and the PFORT Verifier (7) - a program which checks for concurrence with the PFORT subset. A dialect of FORTRAN that is acceptable to most compilers is "Compatible Fortran" (8).

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Another direction aimed at facilitating portability involves the use of a program (pre-processor) to write the FORTRAN. Two examples are Ratfor (9) and Efl (10). A variant of Ratfor - Ratmac (11) - a combination of Ratfor and a macroprocessor language (9), was the programming language used for the NRCC's cooperative computer code generation project for crystallography. This project was organized to develop a well documented and portable computer program to perform multiple isomorphous replacement (MIR) heavy atom phasing of macromolecular phasing.

The MIR workshop accentuated the need for standardization and good programming practice because of the cooperative nature of the program writing. The participants agreed to follow structured programming practice, to employ software tools (12), and to establish common data and parameter transfer conventions (data interfaces) to enable the simultaneous development of separate modules. A key to the success of the program development and a comparable effort in progress in quantum chemistry is modularity - an inherent characteristic of structured programming.

STATISTICAL MECHANICS AND MACROMOLECULAR SCIENCE

A clear trend that emerged from NRCC interaction with researchers in statistical mechanics and macromolecular science was a strong emphasis on computer simulations of increasingly realistic systems. This is evident from the types of problems for which support was sought through the NRCC which included modeling of surface phenomena, multi-phase systems, and long-range interactions, and the rigorous computation of potential energy surfaces using quantum-chemical methods.

At least three NRCC workshops contained principal components of simulation studies. Their titles are descriptive of the subject matter and were: "Stochastic Molecular Dynamics," (13) "The Problem of Long-Range Forces in the Computer Simulation of Condensed Media," (14) and "The Computer Simulation of Organic and Biological Molecules" (15).

Another indication of the rising interest in computer simulation was the relatively large number of requests for the NRCC's simulation program CLAMPS (CLassical Many Particle Simulator) written by David Ceperley of the NRCC. It is a program package that uses five simulation methods (molecular dynamics, Langevin dynamics, Monte Carlo, polymer reptation, and Brownian dynamics) to generate configurations distributed according to the Boltzmann distribution. This program and other NRCC software holdings are presently available from the National Energy Software Center located at Argonne National Laboratory.

More recently, the incorporation of quantum mechanics into simulation studies has emerged as an interesting avenue with the development of quantum Monte Carlo. This method has been applied to the electron gas with encouraging results (16). Applications to atoms and molecules are in progress at the NRCC.

Computer simulation is an area of large computer use and, because of the relative brevity and simplicity of the repetitive time-consuming step of the method, the subject of a variety of performance comparisons on different machines. Earlier findings are recorded by Chester, et al. (17); a recent study is reported by Ceperley (18) for a liquid molecular dynamics simulation.

COLLISION DYNAMICS

With the impact of lasers and the goal of enhancing reaction rates through knowledge of preferred state-to-state mechanisms, there is much theoretical interest in the computation of cross sections and rates of collisional processes. In response to NRCC inquiries on priority activities in collision dynamics, a workshop was organized to assess the comparative merits of algorithms for quantum inelastic scattering. Representative problems were developed by L. Thomas of the NRCC to test current algorithms on the same computer (chosen for convenience to be the CDC 7600). Details of the tests, and the performance of different algorithms are contained in the two-part proceedings volumes of the workshop (19). An immediate product of the testing was the identification that a hybrid of two efficient algorithms could likely outperform any of the algorithms tested. The hybrid code was quickly constructed by developers of the separate codes, tested and found to yield the anticipated efficiencies. It has been announced in the Daresbury (England) Laboratory's CCP (Collaborative Computational Projects) NEWS that a similar project is planned by the CCP6 (Heavy Particle Dynamics) group for the CRAY-1 computer with initial effort focused on the atom-diatom problem.

GRAPHICS

The results of computer studies are initially produced as compilations of numbers from which the theoretical chemist must extract useful chemical information. To this end, computer graphics can greatly help to produce a coherent picture to represent the results of molecular calculations. Such pictures allow the investigator to view and interact with data and models in a meaningful way in order to evaluate the results of computer calculations and establish patterns in these results that may point the way to further investigations.

A high performance molecular graphics facility has the capability of displaying in spatial terms the two- and three-dimensional results of molecular calculations. In addition, it has the capability for demonstrating the time-dependent behavior of dynamic simulations and the capability of modeling and manipulating molecular structures and assemblies in order to understand the often complex interrelationships that govern their properties and interactions.

The development of a high performance molecular graphics facility is an active area of research at the NRCC. The approach taken at the NRCC has been to develop a general purpose graphics language as a tool for chemical application of computer graphics. Other graphics facilities have developed systems which are oriented heavily toward one particular task, thus restricting the exploration of novel graphics applications. The GRAMPS (GRAphics for the Multi-Picture-System) language developed at the NRCC has proven to be a useful tool in the application of computer graphics in a wide variety of chemical computer studies (20).

In the past year, GRAMPS has been used successfully to explore information resulting from studies in crystallography, quantum mechanics, and Monte Carlo simulations of polymer dynamics. As a tool in crystallography, GRAMPS has been used to construct and manipulate models of the TBSV (Tomato Bushy Stunt Virus) particle in order to understand the nature of the protein subunit flexibility and interactions in the process of self-assembly (21). Using capabilities built into GRAMPS, synonyms of the viral protein subunit were created and transformed by appropriate symmetry axes in order to obtain a full icosahedral virus particle. Interactive manipulation of one subunit is echoed in each of its synonyms, while full icosahedral symmetry is maintained. This technique has been used to explore the types of motion available to the viral protein subunits within the packing constraints of the particle geometry. It should be noted that, since translational symmetry can be incorporated into such a procedure, GRAMPS can be applied to aid crystallographers in interactively examining crystal packing problems.

In the field of quantum chemistry, GRAMPS has been used to investigate the four-dimensional potential energy surface for the $O + H_2$ system (22). The four dimensions describing the triatomic system were the H-H distance, the O to H-H center-of-mass distance, the H-H-O angle, and the potential energy value. The surface was represented as a series of three-dimensional surfaces, each having a fixed, but different H-H-O angle. Using GRAMPS, individual three-dimensional frames from the complete series of plots are available under control of a dial, thus allowing real-time investigation of a four-dimensional surface. In this way, a vast amount of chemical information is available in an easily understood form.

The results of stochastic simulations of polymer chain dynamics have been displayed, showing the motion of the polymer subunits throughout the course of a simulation (23). By seeing the motion of the polymer chains and the effect of polymer entanglements on the dynamic motion, it was possible to deduce that the polymer model used was physically reasonable.

Finally, GRAMPS has been used as a tool for investigating the effects of varying some geometrical parameters of the double helical structure of A-DNA. A model of A-DNA was constructed from molecular line drawing models of ribose and of four nucleotide bases. Two torsion angles in the ribose backbone were dynamically varied under the control of a dial. The global effect of changes in these two torsion angles was to effect an unwinding of the 20 base pair double helical model.

Proposed projects using GRAMPS include interactively fitting protein structures into three-dimensional electron density maps obtained from crystal studies, and modeling reaction pathways calculated from quantum mechanical studies of transition states. The general-purpose graphics facility developed at the NRCC has shown itself to be useful in a variety of chemical applications and is expected to be applicable to many other projects.

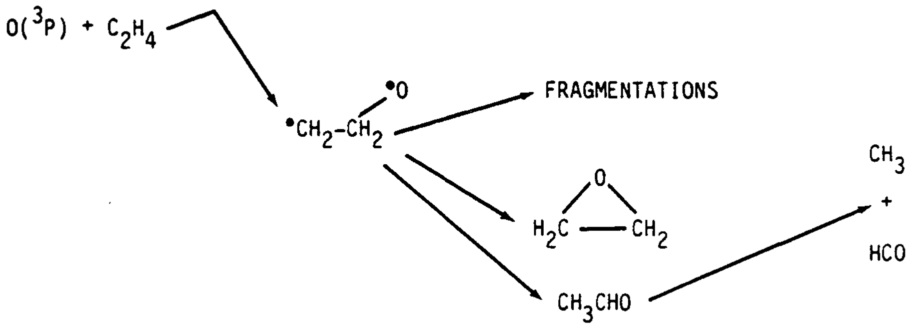
QUANTUM CHEMISTRY

Recent advances in computational techniques have made quantum mechanical methods a powerful tool for the study of chemical reactions. Particularly noteworthy are the new developments in multi-configuration Hartree-Fock (MCHF) (24) and configuration interaction (CI) (25) wavefunction calculations, and the use of gradient techniques (26-29) for the description of potential energy surfaces. In many bond breaking and bond formation processes the Hartree-Fock (HF) model breaks downs. In such cases a MCHF wavefunction can provide a qualitatively correct description of the reaction mechanism. Extended CI calculations are necessary for quantitatively accurate reaction energies. Gradient techniques are extremely useful for the description of potential energy surfaces because they make possible the rapid determination of equilibrium structures, transition state structures, and force fields for HF, MCHF, and CI wavefunctions, thus providing a complete characterization of the geometrical and electronic changes associated with chemical reactions. We have used these techniques to study some elementary steps of the reaction of O + C_2H_4.

Reaction of Oxygen Atoms with Ethylene

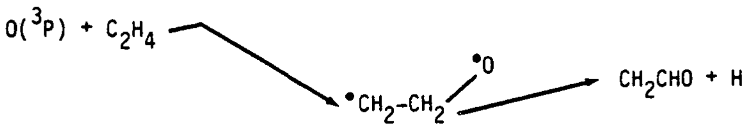
The reaction of oxygen atoms with olefins plays an important role in combustion processes and photochemical oxidation. Although global reaction rates have been measured for many of these reactions, very little is known about the elementary reactions and the free radical intermediates formed in these important reactions.

The mechanism originally proposed by Cvetanović (30) involves the formation of a short lived diradical CH_2CH_2O from the addition of $O(^3P)$ to the double bond. The diradical undergoes subsequent unimolecular reactions such as formation of "hot" epoxide, hydrogen atom migration to form "hot" acetaldehyde, and other pressure independent fragmentations (I):



(I)

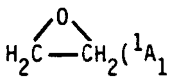
Direct observation of CH_3, HCO (95%), and CH_2CO (4%) by Kanofsky and Gutman (31) was interpreted as a verification of Cvetanović's mechanism. However, several recent experiments by Lee (32) and others (33-35) challenge this mechanism and suggest that the vinoxy radical CH_2CHO is a primary product of the O + C_2H_4 reaction



(II)

Correlation Diagram. The energy diagram shown in Fig. 1 has been obtained with CI wavefunctions (single and double excitations from the HF configurations) and by accounting for polarization function effects using the procedure suggested by Bargon, et al. (36), which assumes the additivity of the polarization function correction and of the electron correlation effect. Table I gives some selected calculated and experimental enthalpies of reaction.

TABLE 1. Selected Enthalpies of Reaction ΔE(kcal/mol)

	Calc.^{a}	Expt.
$O(^3P) + C_2H_4 \rightarrow$  $(^1A_1)$	-69.4	- 80.
$O(^3P) + C_2H_4 \rightarrow CH_3CHO(^1A_1)$	-99.9	-112.
$O(^3P) + C_2H_4 \rightarrow CH_3(^2A_1) + HCO(^2A')$	-23.0	- 27.5
$O(^3P) + C_2H_4 \rightarrow H_2CCO(^1A_1) + H_2$	-68.8	- 82.

a. $\Delta E = \Delta E(HF;DZ) + [\Delta E(SDQHF;DZ) - \Delta E(HF;DZ)] + [\Delta E(HF;DZP) - \Delta E(HF;DZ)]$

SDQHF denotes single and double excitations from a Hartree-Fock reference wavefunction and quadruple excitations estimated from Davidson's correction. DZ denotes double zeta basis set and DZP indicates the further addition of polarization functions to the DZ basis set.

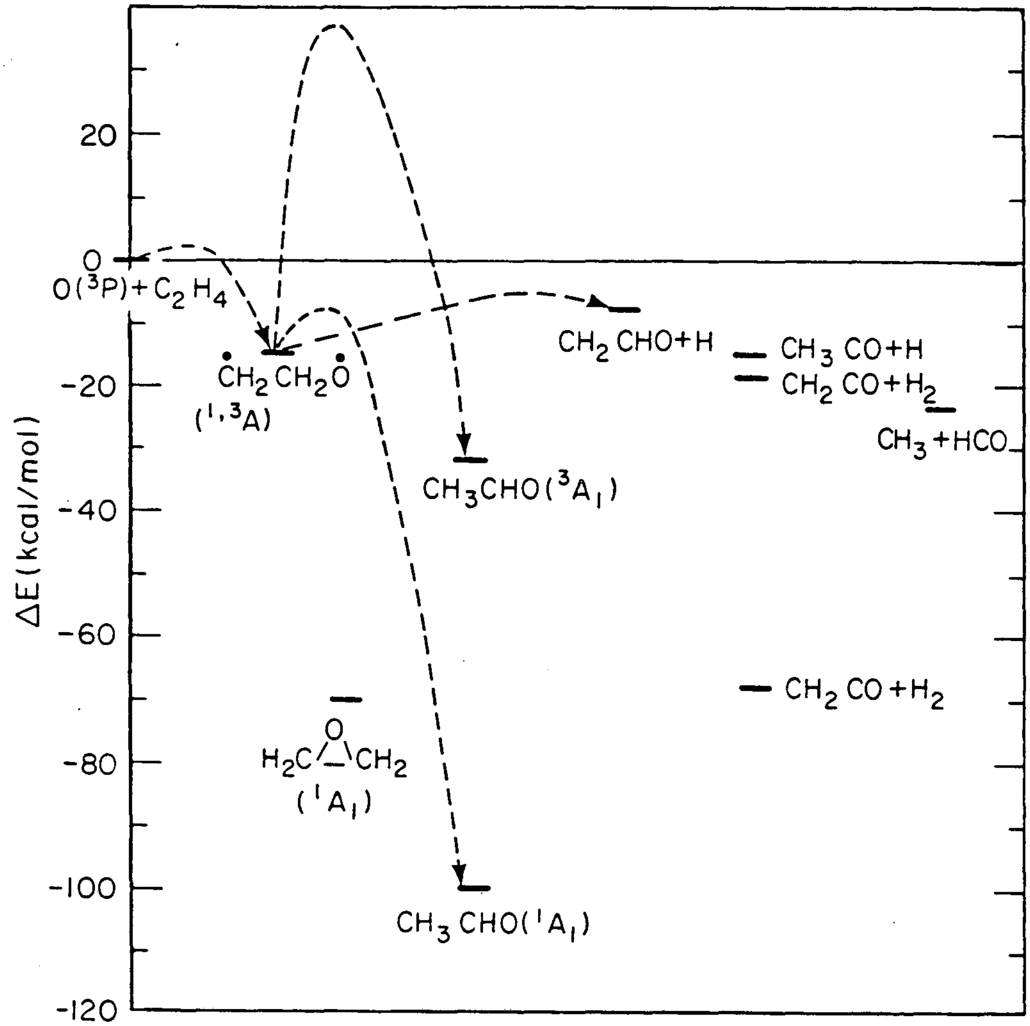


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Fig. 1. Correlation diagram for $O(^3P)$ + C_2H_4.

The dotted lines of Fig. 1 correspond to energy curves of selected elementary steps. In these elementary reactions the structures of the transition states have been fully characterized using HF or MCHF wavefunctions. The configurations included in the wavefunctions allow a proper description of the reactants, transition states, and products of the reactions. In all cases the orbitals active during the course of the reaction (i.e., involved in bond breaking and bond formation) are selected, and the active electrons are distributed in all possible ways among the active orbitals (complete active reaction space wavefunctions). The most important conclusions for each of the indicated paths follow:

i. $O(^3P) + C_2H_4 \longrightarrow {}^{\cdot}CH_2\text{-}CH_2\text{-}O^{\cdot}\ (^3A'')$. This reaction can be described with three electrons in three active orbitals. The transition state has C_s symmetry, not C_{2v} as might be expected. The energies for the reaction calculated with the MCHF wavefunctions are shown in Table 2. Further improvements of the relative energies require polarization functions and extended CI calculations using the MCHF wavefunction as a reference.

TABLE 2. Activation energy (E_a) and enthalphy of reaction (ΔE) for $O(^3P) + C_2H_4 \longrightarrow {}^{\cdot}CH_2\text{-}CH_2\text{-}O^{\cdot}(^3A'')$

	E_a(kcal/mol)	ΔE(kcal/mol)
MCHF(MB)	+ 15.8	- 1.7
MCHF(DZ)	+ 16.0	+10.5
Expt.[30]	+ 1.0	-

ii. $^{\cdot}CH_2\text{-}CH_2\text{-}O^{\cdot}(^{1,3}A') \longrightarrow CH_3CHO(^{1,3}A_1)$. The HF configuration describes properly the H-atom migration on the triplet surface. Two configurations are required for the singlet surface, as the reactant $^{\cdot}CH_2CH_2O^{\cdot}$ has two unpaired electrons, and the product $CH_3CHO(^1A_1)$ is a closed shell molecule. There is a high barrier (~ 50 kcal/mol) to H-atom migration on the triplet surface, and a small barrier (less than 10 kcal/mol) on the singlet surface. For the triplet transition state, the CI wavefunction based on the generalized valence bond orbitals (GVB/CI) describes some important correlation effects. A significantly lower barrier is obtained with a DZP basis set than with a DZ one. Further improvements of the energy barrier calculations require an extended CI wavefunction with DZP basis set. The results of Table 3 are semiquantitative.

TABLE 3. Activation energy (E_a) and enthalpy of reaction (ΔE) for

(1) $^{\cdot}CH_2CH_2O^{\cdot}(^3A'') \longrightarrow CH_3CHO(^3A_1)$

	E_a(kcal/mol)	ΔE(kcal/mol)
HF(MB)	+ 81.8	-10.9
HF(DZ)	+ 64.5	- 5.7
HF(DZP)	+ 57.0	- 5.5
GVB(DZ)	+ 68.7	- 1.6
GVB/CI(DZ)	+ 56.5	- 7.2

(2) $^{\cdot}CH_2CH_2O^{\cdot}(^1A') \longrightarrow CH_3CHO\ (^1A_1)$

	E_a(kcal/mol)	ΔE(kcal/mol)
MCHF(DZP)	+ 10.3	~ -80.0

iii. $CH_2\text{-}CH_2\text{-}O(^3A'') \longrightarrow CH_2CHO(^2A'') + H(^2S)$. The reaction, $O(^3P) + C_2H_4 \longrightarrow CH_2CHO + H$, proceeding through the formation of the diradical CH_2CH_2O, followed by H-atom elimination, involves six electrons and six orbitals (189 configurations).

TABLE 4. Energetics of formation of vinoxy radical

	$O + C_2H_4$	$^{\cdot}CH_2CH_2O^{\cdot}$	TS	$CH_2CHO + H$
MCHF(MB)	0.0	- 2.7	+48.0	+42.0
MCHF(DZ)	0.0	+ 9.2	+31.8	+20.8

The enthalpies of reaction calculated with the MB and DZ basis sets are not in agreement with the more reliable results of Fig. 1. Here too a DZP basis set is required for quantitative accuracy. However, the small energy difference between the transition state (TS) and the products $CH_2CHO + H$ is anticipated to be qualitatively correct.

The structure of the vinoxy radical CH_2CHO. The $^2A''$ ground state of the vinoxy radical CH_2CHO results from the resonance interaction of $CH_2{=}CH\text{-}O^{\cdot}$ and $^{\cdot}CH_2\text{-}CH{=}O$. It is a three-electron delocalized π system. In addition there exists a $^2A'$ structure corresponding to $CH_2{=}CH\text{-}O^{\cdot}$; see Fig. 2. A MCHF description involving the π electrons only for the $^2A''$ and $^2A'$ structures gives the excitations energies presented in Table 5.

TABLE 5. Low Lying Electronic States of CH_2CHO (eV)

	MCHF(MB)	MCHF(DZ)	Expt.[34]
$1^2A''$	3.02	3.22	3.57
$^2A'$	0.20	0.54	0.99
X^2A''	0.00	0.00	0.00

Conclusions of oxygen-ethylene study.

i. Vinoxy radical CH_2CHO: the present MCHF calculations predict a near infrared electronic transition $X^2A'' \longrightarrow {}^2A'$ recently confirmed by experiment.

ii. $O + C_2H_4 \longrightarrow CH_2CH_2O$: the transition state has C_s symmetry and not C_{2v} as would be expected by symmetric positioning of O-atom with respect to the double bond.

iii. $CH_2CH_2O \longrightarrow CH_3CHO \longrightarrow CH_3 + HCO$: the energy barrier for H-atom migration on the triplet potential energy surface is ~50 kcal/mol, and less than 10 kcal/mol on the singlet potential energy surface. Formation of CH_3CHO must proceed through an intersystem crossing in ${}^\bullet CH_2-CH_2-O^\bullet$.. Vibrationally "hot" acetaldehyde can decompose unimolecularly to form CH_3 + HCO.

iv. $CH_2CH_2O \longrightarrow CH_2CHO + H$: preliminary calculations indicate a small barrier to H-atom elimination.

Details of this study will be published shortly (37,38).

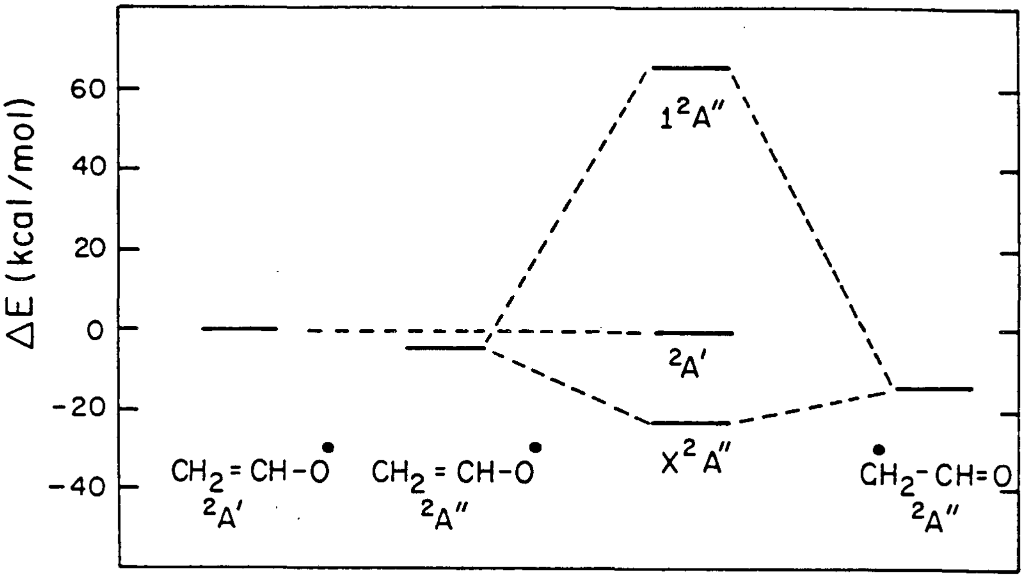

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Fig. 2. Resonance interaction diagram for vinoxy radical structures.

Technical considerations. To extend the capabilities of the HONDO computer code used in the oxygen atom-ethylene study and to carry out the calculations, we had access to a large (CDC7600) computer mainframe and to a midicomputer (DEC VAX 11/780). For CPU intensive tasks such as integral calculation the CDC7600 is found to be 22 times faster than the VAX. For tasks requiring a large memory the ratio can be even more favorable for the CDC7600 because of the virtual memory paging of the VAX with the present software. However, the relatively small physical memory of the CDC7600 seriously limits the size of problems which can be handled.

During the debug stage of code development, it is not unusual to run test jobs of 1/2 to 1 minute of CPU time on the CDC7600. Smaller tests may not always exercise all the features of the code. In a multi-task environment, an equivalent 15-20 minute (CPU) job on the VAX leads to a much longer waiting period for output.

The memory limitations of the CDC7600 made it necessary to run most of the MCHF calculations on the VAX. A typical case is the $CH_2CH_2O \longrightarrow CH_2CHO + H$ reaction with a DZ basis set (35 basis functions, 189 configurations). An energy plus gradient calculation takes 7 CPU hours on the VAX with the present code. A geometry optimization or saddle point search requires 5 to 8 energy plus gradient evaluations. In a multi-task environment, the job could be in the machine for up to 6-7 days. MCHF calculations with more than 50 basis functions are not feasible on the VAX with the present version of the code because they would require four to five times the CPU time of a 35 basis function calculation.

It is important to note that the present version of the HONDO code is not optimal in many tasks, and that no significant effort has been made to optimize it for the VAX computer. However, it is clear that the present capabilities of the code are much greater than two years ago at the start of the NRCC software library.

Final Remarks on Quantum Chemistry. The level of sophistication of models used in quantum chemical studies is steadily increasing. New techniques are presently under development which will open new directions of chemical research. The Hartree-Fock calculations of yesterday on closed-shell molecules have been replaced by multiconfiguration Hartree-Fock calculations of radical species. Seen in this light, there is a continuing need for faster computers with larger memory capabilities.

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