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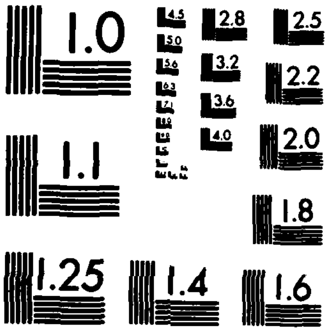

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Report Number ONR-NR093064-TR4

SUMMARY

ANNUAL REPORT

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF CATIONIC POLYMERIZATION

and

THEORETICAL PREDICTION OF CRYSTAL DENSITIES

and

DECOMPOSITION PATHWAYS OF ENERGETIC MOLECULES

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configuration interaction
coupled-cluster theory
crystal and polymer orbitals
intermolecular interactions
nitroexplosives

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

I. Ab-initio crystal orbitals and polymer orbitals
II. Ab-initio coupled cluster program
III. Ab-initio quantum chemical calculations and electrostatic molecular potential contour maps for cationic polymerization
IV. Prediction of crystal density
V. Ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes
VI. Ab-initio configuration interaction calculations on the CH_3-NO_2

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) decomposition pathway of nitromethane

VII. Ab-initio configuration interaction calculations on RDX

VIII. Conversion of our programs to vector supercomputers, CYBER and CRAY

We have made significant progress this year in two new program endeavors which will impact all areas of our ONR Power Programs research on energetic compounds.

I. We have so far completed the analysis, coding and testing of the integral and SCF portions of the crystal orbital part of the program and the analysis and some coding for the polymer orbital part. We meshed into this new POLYCRYST program, as options, all of our desirable computational strategies for ab-initio calculations on large molecules.

II. Ab-initio coupled-cluster program including multireference determinants and a new original repetitive method, based either on localized orbitals or conventional delocalized canonical orbitals.

Our strategy in this part of the research has been to mesh together with configuration interaction the desirable features of coupled-cluster theory. We have carried out preliminary calculations on RDX.

III. We have continued optimizing geometries and generating electrostatic molecular potential contour maps (EMPC) maps for new monomers of interest experimentally.

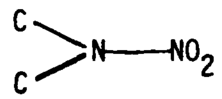
This past year we have also been working to develop methodology for more quantitative predictions of relative polymerization ratios. Thus, we have developed and implemented methods to calculate the volume, shape and accessibility of isopotential EMPC contours, and are developing a strategy for comparing electrophilicities for the propagation step.

IV. Using our CRYSTAL program, electrostatic and electric field terms based on the molecule RDX, and atom class-atom class potentials from CH_3NO_2, and a series of diatomic dimers, we have predicted the density of RDX to within 0.1%. This method then holds promise for predicting unit cell parameters of large explosives.

V. We have continued to carry out ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes to generate electrostatic molecular potential contour (EMPC) maps around these polynitropolyhedranes and polynitropolyazapolyhedranes. These EMPC maps appear to indicate that the character of the nitro groups may change as a function of the degree of nitration, and they also may prove useful in understanding how these molecules will pack in crystals.

VI. Ab-initio configuration interaction calculations using multireference determinants have been carried out for much of the CH_3-NO_2 decomposition pathway of nitromethane. For each point, in the order of 800,000 configurations were generated and sifted using perturbation theory for the most important.

VII. Preliminary CI calculations were carried out on RDX at equilibrium considering the molecular orbitals centered primarily on a



portion of the skeleton as a prototype for the N-NO_2 decomposition. Even at equilibrium, a multireference determinant character on the NO_2 group was found--similar to that in CH_3-NO_2.

VIII. We have gotten access to CYBER 205 and CRAY time. We are the process of converting our programs to both of these machines.

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF CATIONIC POLYMERIZATION AND THEORETICAL PREDICTION OF CRYSTAL DENSITIES AND DECOMPOSITION PATHWAYS OF ENERGETIC MOLECULES

Joyce J. Kaufman, Principal Investigator

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QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF CATIONIC POLYMERIZATION AND THEORETICAL PREDICTION OF CRYSTAL DENSITIES AND DECOMPOSITION PATHWAYS OF ENERGETIC MOLECULES

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CONCISE SUMMARY

→ This study involves:

I. Ab-initio crystal orbitals and polymer orbitals;
II. Ab-initio coupled cluster program,
III. Ab-initio quantum chemical calculations and electrostatic molecular potential contour maps for cationic polymerization;
IV. Prediction of crystal density,
V. Ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes,
VI. Ab-initio configuration interaction calculations on the CH_3-NO_2 decomposition pathway of nitromethane;
VII. Ab-initio configuration interaction calculations on RDX; and
VIII. Conversion of our programs to vector supercomputers, CYBER 205 and CRAY.

We have made significant progress this year in two new program endeavors which will impact all areas of our ONR Power Programs research on energetic compounds.

I. Ab-initio crystal orbitals and polymer orbitals

This program will enable one to answer such questions as:
How do the occupied and virtual molecular orbital energy levels and the bond strengths of a molecule change from the isolated molecule when the molecule is in a crystal?
What is the bonding between molecules in a crystal?
These both affect properties important in explosives.
How does the bonding change within an energetic pendant group and between the pendant group and the backbone between a monomer and a polymer?
We have so far completed the analysis, coding and testing of the integral and SCF portions of the crystal orbital part of the program and the analysis and some of the coding for the polymer orbital part of the program. We meshed into this new POLY-CRYST program, as options, all of our desirable computational stategies for ab-initio calculations on large molecules.

II. Ab-initio coupled cluster program including multireference determinants and a new original repetitive method, based either on localized orbitals or conventional delocalized canonical orbitals.

Our large-scale ab-initio multireference determinants configuration interaction calculations on the decomposition of nitromethane CH_3-NO_2 decomposition pathway indicated that not only were there the two determinants found at the equilibrium geometry (located on the NO_2 group), but also that as the C-N bond was broken additional determinants became

CONCISE SUMMARY (cont.)

important.

Our strategy in this part of the research has been to mesh together with configuration interaction the desirable features of coupled cluster theory.

Thus, for calculations of decomposition pathways of energetic molecules with NO_2 groups, multireference determinants will be necessary within any many-body perturbation theory or coupled cluster theory.

We have completed the analysis, coding and testing of a coupled cluster program based either on localized orbitals or delocalized orbitals and have carried out preliminary calculations on RDX.

We have so far completed the analysis, coding and testing for the linear coupled cluster terms based on multireference determinants and have carried out preliminary calculations on RDX. We are now working on the implementation of the higher order terms. However, since we can include any number of multireference determinants in our starting wave function, this should ameliorate the necessity for many or most of the higher order terms. We will be testing this hypothesis.

Another strategy is to apply the T_1 and T_2 operators repetitively, each time on the improved wave function from the previous cycle. This will generate the higher order terms but has the advantage of keeping down the size of the equations to be solved. We have completed the analysis, coding and testing of the strategy and have carried out preliminary calculations on RDX.

We have also continued our research and made gratifying progress in

III. Ab-initio quantum chemical calculations and electrostatic molecular potential contour maps for cationic polymerization

We have continued optimizing geometries and generating electrostatic molecular potential contour (EMPC) maps for new monomers of interest experimentally. Our previous results had illustrated vividly that these EMPC maps were capable of predicting reliably the basicity of even hypothetical monomers prior to their synthesis. The initiation step in the cationic polymerization of cyclic ethers is governed by the basicity of these monomers and our EMPC maps predicted reliably the rank order of polymerization and even optimal copolymer candidates.

This past year we have also been working to develop methodology for more quantitative predictions of relative polymerization ratios. This is complicated by the fact that there are two steps in the polymerization: initiation--proportional to basicity and propagation--considered by experimental polymer chemists to be influenced by the electrophilicity of the propagating ring opened carbocation. We had already shown that these two steps are influenced in opposite and competing directions by the character of the substituent groups. We had also shown that initiation was a dominant step. Thus we have developed

CONCISE SUMMARY (cont.)

and implemented methods to calculate the volume, shape and accessibility of isopotential EMPC contours. We are now carrying out such calculations to compare against experimental data. We are also developing a strategy for comparing electrophilicities for the propagation step.

IV. Prediction of crystal density

We have been quite successful in this endeavor during the past year.

Using our CRYSTAL program, we predicted the unit cell volume of CH_3NO_2 to within 4.27% and hence the density to within -4.27% using ab-initio atom class - atom class potential functions from energy partitioned ab-initio calculations on CH_3NO_2 plus short range atom - atom terms from a series of diatomic dimers.

Certain of the terms such as the multipole contributions to the electrostatic term and the electric field for the polarization term are recalculated explicitly each time for each change in unit cell parameter from the wave function of the molecule.

Even more gratifying is that we predicted the unit cell dimensions of RDX to within -1.0 (a), 1.5 (b), -0.6 (c)% and thus the density to within 0.1%, employing the same strategy but using the ab-initio atom class-atom class potentials from CH_3NO_2 and the diatomic dimers. This then holds promise for predicting unit cell parameters of large explosives. Such calculations are very sensitive to the goodness of the potentials.

V. Ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes

We have continued to carry out ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes. From these wave functions we have been generating electrostatic molecular potential contour (EMPC) maps around these polynitropolyhedranes and polynitropolyazapolyhedranes. These EMPC maps appear to indicate that the character of the nitro groups may change as a function of the degree of nitration. Also these EMPC maps may prove useful in understanding how these molecules will pack in crystals.

Molecules which have a number of nitro groups around their peripheries could scarcely be expected to approach each other closer than a zero isopotential contour if the signs of the EMPC contours of the adjoining molecules are the same. On the other hand, if the molecules are surrounded by molecules with both positive and negative EMPC contours, the molecules may try to orient themselves in a crystal having regions of positive EMPC contours around one molecule adjoining regions of negative EMPC contours around the other molecule.

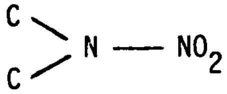
CONCISE SUMMARY (cont.)

VI. Ab-initio configuration interaction calculations on the CH_3-NO_2 decomposition pathway of nitromethane

Ab-initio configuration interaction calculations using multireference determinants have been carried out for much of the CH_3-NO_2 decomposition pathway of nitromethane. For each point in the order of 800,000 configurations were generated. Using a perturbation procedure the energy contribution of each configuration was calculated. All configurations contributing an energy higher than a chosen threshold were included in the CI wave function to be solved. Then an extrapolation was performed to take into account the energy contributions of the configurations not included explicitly. This was then followed by a Davidson type correction for size-consistency.

VII. Ab-initio configuration interaction calculations on RDX

Preliminary CI calculations were carried out on RDX at equilibrium considering the molecular orbitals centered primarily on a



portion of the skeleton as a prototype for the N-NO_2 decomposition. Even at equilibrium a multireference determinant character on the NO_2 group was found - similar to that in CH_3-NO_2. Thus, it appears to be a general characteristic of all aliphatic nitroexplosives.

Several major invited papers have been presented on our polymer research at the 1983 Gordon Conference on Polymers and at the 1983 NATO Advanced Study Institute on Quantum Theory of Polymers: Solid State Approaches. Our plenary lecture at the NATO Advanced Study Institute also included results using our CRYSTAL program on prediction of crystal densities. An invited paper on the crystal results was also presented at the Sanibel International Symposium on Molecular and Solid State Theory and Computational Quantum Chemistry.

Papers on the polymer, crystal, polynitropolyhedrane and nitromethane CI results were also presented at the National American Chemical Society and American Physical Society Meetings.

Papers on several of the above topics are already accepted for publication and in press.

VIII. Conversion of our programs to vector supercomputers, CYBER 205 and CRAY

The quantum chemical problems we are investigating involve large scale calculations on large systems, both with many atoms and/or with many configurations or simultaneous equations to be solved. We have gotten access to CYBER 205 time and to CRAY time. The CYBER 205 has two million 64 bit words in real memory plus virtual memory. The CRAY has one million words of real memory. We are in the process of converting our programs to both of these machines.

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF CATIONIC POLYMERIZATION AND THEORETICAL PREDICTION OF CRYSTAL DENSITIES AND DECOMPOSITION PATHWAYS OF ENERGETIC MOLECULES

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I. Ab-initio crystal orbitals and polymer orbitals

We have so far completed the analysis, coding and testing of the integral and SCF portions of the crystal orbital part of the program and the analysis and some of the coding for the polymer orbital part of the program. We meshed into this new POLY-CRYST program, as options, all of our desirable computational strategies for ab-initio calculations on large molecules.

A. Methodology

1. Major Features

This technique permits one to calculate ab-initio quantum chemical crystal orbitals and polymer orbitals making use of the translational symmetry in a crystal and translational and/or translational-rotational symmetry in a polymer.

Main features of the ab-initio SCF portion of the crystal orbital part of the program method:

- Fully Ab-inito
- Full use of translational symmetry
- Analogous to molecular Hartree-Fock-Roothaan Method
- No theoretical problems in approaching Hartree-Fock limit (All numerical difficulties can have arbitrarily strict convergence criteria)
- General in 1, 2 or 3 dimensions

Differences from the ab-initio SCF molecular method:

- Periodic Gaussians replace Gaussians in basis set
- Additional quantum number present in orbital description
- Gross atomic orbital populations and total overlap populations in molecule reflect influence of surrounding molecules.

2. Problem Definition

Specify the location of the molecules within one unit cell. Specify a set of lattice vectors $\{\vec{R}\}$ which describe the translation of the primary unit cell to all equivalent positions. Include enough unit cells in the integrals until the interactions are negligible. Calculation of the wavefunction within one unit cell is now sufficient since all unit cells are equivalent. The cell-cell interactions are already included in the integrals.

a. Introduction of $\vec{k}$ into the Problem

As an electron moves in the periodic potential of the crystal, the difference between unit cells is only due to the phase difference. This can be introduced into our formalism along with the periodicity by introducing phase factors of $e^{-i\vec{k}\cdot\vec{R}}$ into our functions. It is not convenient to deal directly with a continuous variable in our calculations. In practice we evaluate the crystal properties on a mesh of discrete $\vec{k}$ points which can be as fine as necessary to display all the features of the band structure.

b. New Quantum Number $\vec{k}$

It is well know that bringing identical atoms together causes a splitting of the degeneracy of the orbital levels in the formation of molecular orbitals. Similarly, assembling identical molecules causes a "smearing out" of the molecular orbital levels into energy bands, as the energies of the crystal orbitals are usually known. The position of an electron within the band is described by the continuous variable $\vec{k}$, representing the "crystal momentum" or "wavenumber" of the electron. Because of the translational symmetry, $\vec{k}$ can be restricted without loss of generality to the first Brillouin Zone (first unit cell in momentum space.)

The form of our periodic basis function is now:

$$\sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \chi_\mu(\vec{r}+\vec{R})$$

where $\vec{R}$ runs in principle over all lattice vectors of the crystal. Only cells with interactions above our threshold must be included.

For $\chi_\mu(\vec{r})$ we can choose any convenient functions, such as Gaussian- or Slater-type orbitals. We choose a sum of primitive cartesian Gaussians.

The form of the answer is

$$\phi_{n\vec{k}}(r) = \frac{1}{\sqrt{N}} \sum_{\vec{R}}^{N} \sum_{\mu}^{B} e^{-i\vec{k}\cdot\vec{R}} c_{n\mu\vec{k}} \chi_\mu(\vec{r}+\vec{R})$$

where N is the number of cells and B is the size of the basis set in the primary unit cell. The $\vec{k}$ dependence is indicated by subscripts on ϕ and c. The variation within $\vec{k}$ is smooth. This band holds 2N electrons, so the normalization of $\frac{1}{\sqrt{N}}$ gives the correct number per unit cell.

c. Hartree-Fock crystal orbital equations and matrix elements

The Hartree-Fock crystal orbital equations are

$$\overleftrightarrow{H}_{n\vec{k}}\;\vec{C}_{n\vec{k}} = E_{n\vec{k}}\;\vec{\vec{S}}_{k}\;\vec{C}_{n\vec{k}}$$

in matrix form. The overlap matrix elements are

$$S_{\mu\nu\vec{k}} = \sum_{\vec{R}}^{N} e^{-i\vec{k}\cdot\vec{R}} \langle \chi_{\mu}(\vec{r}) \mid \chi_{\nu}(\vec{r})\rangle$$

and the Hamiltonian matrix elements are

$$\begin{aligned}
H_{\mu\nu\vec{k}} = \sum_{\vec{R}}^{N} e^{-i\vec{k}\cdot\vec{R}} \Big\{ & \langle\chi_{\mu}(\vec{r}) \mid \frac{-\nabla^{2}}{2} \mid \chi_{\nu}(\vec{r}+\vec{R})\rangle \\
& + \sum_{I}^{\text{cell}} \sum_{\vec{R}'}^{N} \langle \chi_{\mu}(\vec{r}) \mid \frac{-Z_{I}}{|\vec{R}'_{I} - \vec{r}|} \mid \chi_{\nu}(\vec{r}+\vec{R})\rangle \\
& + \sum_{\vec{R}_1}^{N} \sum_{\vec{R}_2}^{N} \sum_{\gamma\delta} \frac{1}{N} \int_{\substack{\text{Brillouin}\\ \text{Zone}}} d\vec{k}' \sum_{n}^{\text{occ}(\vec{k}')} e^{-i\vec{k}'\cdot(\vec{R}_1-\vec{R}_2)} \qquad c^{*}_{n\gamma\vec{k}'}\, c_{n\delta\vec{k}} \qquad \times \\
& \Big[2\langle\chi_{\gamma}(\vec{r}'+\vec{R}_2)\ \chi_{\mu}(\vec{r}) \mid \frac{1}{|\vec{r}'-\vec{r}|} \mid \chi_{\nu}(\vec{r}+\vec{R})\ \chi_{\delta}(\vec{r}'+\vec{R}_1)\rangle \\
& - \langle\chi_{\gamma}(\vec{r}'+\vec{R}_2)\ \chi_{\mu}(\vec{r}) \mid \frac{1}{|\vec{r}'-\vec{r}|} \mid \chi_{\delta}(\vec{r}+\vec{R}_1)\ \chi_{\nu}(\vec{r}'+\vec{R})\rangle\Big]\Big\}
\end{aligned}$$

3. Logic of Crystal Orbital Program

Step 1. Generation of lattice vectors from cell parameters and cell selection criteria.

Step 2. Calculation of real-space one-electron integrals for all cases where one function is in the primary unit cell.

Step 3. Calculation of real-space two-electron integrals for all cases where one function is in the primary unit cell.

Step 4. For each $\vec{k}$-point, obtain the integrals for the periodic basis functions. The pieces from different cells must be collated and phase factors introduced.

Step 5. Input initial coefficients and k-occupation.

Steps 6-9 are SCF cycle

Step 6. Form density matrix by 3-dimensional numerical integration over $\vec{k}$.

Step 7. Form Fock matrix for each $\vec{k}$.

Step 8. Diagonalize each Fock matrix.

Step 9. Obtain new coefficients, test for convergence and do bookkeeping.

4. Remaining Program Development and Implementation

a. Population Analysis

We have done the analyses and are now implementing the population analysis portion. The results of the population analyses gives the gross atomic charges on the atoms and the total overlap popualtional TOP's between atoms (both intra and intermolecular). These TOP's indicate whether the intramolecular bonding is strengthened or weakened when a molecule is placed in a crystal or a polymer. These TOP's also indicate the strength of intermolecular bonding.

b. Properties Package

The analyses has been done for a properties package to calculate atomic and molecular multipole moments. These are important in intermolecular interactions. This section will be implemented.

c. Inclusion of Correlation Energy

We are now giving careful consideration into how best to include correlation effects. At the NATO Advanced Study Institute on Quantum Theory of Polymers: Solid State Approaches last summer, it was suggested that using many-body perturbation theory or coupled cluster theory based on localized orbitals might be the most tractable, fruitful approach.

We had already coded and tested for molecules the coupled cluster approach based either on localized orbitals or on delocalized orbitals in connection with our research on the decomposition of the nitroexplosives. (See next section II). We are now looking into how best to mesh this approach with the crystal orbital / polymer orbital program.

Major credit for this effort is due to Dr. John M. Blaisdell with the collaboration of Dr. P.C. Hariharan.

B. Types of Pertinent Questions Which Can Be Answered With This Method

This program will enable one to answer such questions as:

1. Crystals

How do the occupied and virtual molecular orbital energy levels and the bond strengths of a molecule change from the isolated molecule when the molecule is in a crystal?

What is the bonding between molecules in a crystal?

2. Polymers

How does the bonding change within an energetic pendant group and between the pendant group and the backbone between a monomer and a polymer?

II. Ab-initio coupled cluster program, including multireference determinants and a new original repetitive method, based either on localized orbitals or conventional delocalized canonical orbitals.

A. Introductory discussion

Our strategy in this part of the research has been to mesh together with configuration interaction the desirable features of coupled-cluster theory.

Our large-scale ab-initio multireference determinant configuration interaction calculations on the CH_3-NO_2 decomposition pathway of nitromethane indicated that, not only were there the two determinants found at the equilibrium geometry (located on the NO_2 group), but also C-N bond was broken, additional determinants became important.

Thus, for calculations of decomposition pathways of energetic molecules with NO_2 groups, multireference determinants will be necessary within any many-body perturbation theory or coupled-cluster theory.

We have completed the analysis, coding and testing of coupled-cluster theory based on multireference determinants.

We have completed the analysis, coding and testing of a coupled-cluster program based either on localized orbitals or delocalized orbitals and have carried out preliminary calculations on RDX.

Another strategy is to apply the T_1 and T_2 operators repetitively, each time on the improved wave function from the previous cycle. This will generate the higher order terms but has the advantage of keeping down the size of the equations to be solved. We have completed the analysis, coding and testing of the strategy and have carried out preliminary calculations on RDX.

B. Background and methodology

1. Coupled-cluster method

The coupled-cluster method is an attempt to introduce interactions among electrons within clusters as well as coupling amoung these clusters of electrons and to permit the wave functions to contain all possible disjoint clusters. Coupled-cluster theory had previously been shown by others to be a useful approach to the correlation problems in small and medium size atomic and molecular systems. The coupled-cluster method truncated to first and second order had been used by others in closed and open shell cases.

The question arises, "How important are higher orders, specifically third and fourth order, in the coupled-cluster method?" Previous studies of closed-shell systems had demonstrated that fourth order terms are often chemically significant.

First, the full set of diagrams for closed and open shell systems, including all single and double excitations, was derived originally by Sauté in France (for his doctoral thesis with Professor Laforgue).

Then in our group at the Johns Hopkins University these diagrams were systematically tabulated by Professor Laforgue. Now, in our group Professor Laforgue and Dr. Roszak have expanded coupled cluster theory through third and fourth order, including sets of equations, complete sets of diagrams and the table of matrix elements. This latter has been implemented computationally at the Johns Hopkins University by Dr. Roszak.

In the cluster-type expansion the exact wave function is expressed in the following form:

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle \qquad \text{(II-1)}$$

where $|\Psi\rangle$ represents the wave function in the one-particle model;

$\hat{T}$ is the wave operator and $e^{\hat{T}}$ is the correlation operator. Operator $\hat{T}$ generates one-, two-electron, etc., clusters with

$$T_j = \frac{1}{j} \sum_{n'n''} \langle 1''\ldots j''|t|1'\ldots j'\rangle \prod_{i=1}^{j} X^{+}_{i''} X_{i'} \qquad \text{(II-2)}$$

The matrix elements of T are the unknown numbers which define the formal operator t. The number j corresponds to the number of excitations:

$$T = T_1 + T_2 + T_3 + T_4 + \ldots \qquad \text{(III-3)}$$

T_1: 1-electron excitation operator (only single excitations)

T_2: 2-electron excitation operator (only double excitations)

T_3: 3-electron excitation operator (only triple excitations)

T_4: 4-electron excitation operator (only quadruple excitations)

To make some connection between the coupled cluster wave function of equation (II-1) and more conventional CI (configuration interaction) or MBPT (many-body perturbation theory) expressions for $|\Psi\rangle$, expand the right side of equation (II-1) and collect terms of common excitation level:

$$e^{T}|\Psi\rangle = [1 + (T_1 + T_2 + T_3 + T_4 + \ldots) + \frac{1}{2!}(T_1 + T_2 + T_3 + T_4 + \ldots)^2 + \frac{1}{3!}(T_1 + T_2 + T_3 + T_4 + \ldots)^3 + \frac{1}{4!}(T_1 + T_2 + T_3 + T_4 + \ldots)^4] |\Psi\rangle \qquad \text{(II-4)}$$

By grouping the terms of a given excitation level together, we see that the coupled cluster wave function can be rewritten as

$$e^{T}|\Psi\rangle = (1 + C_1 + C_2 + C_3 + C_4)|\Psi\rangle \qquad \text{(II-5)}$$

where the CI operators C_1, C_2, C_3, C_4, ... are

$$C_1 \approx T_1$$

$$C_2 \approx T_2 + \frac{1}{2!}T_1^2$$

$$C_3 \approx T_3 + \frac{1}{3!}T_1^3 + T_1T_2$$

$$C_4 \approx T_4 + \frac{1}{4!}T_1^4 + \frac{1}{2!}T_2^2 + T_1T_3 + \frac{1}{2}T_1^2T_2 \quad \text{,etc.} \qquad \text{(II-6)}$$

The method has been coded up and tested for

$$e^T = 1 + T_1 + T_2 + T_3 + T_4 + \frac{1}{2}T_1^2 + \frac{1}{2}T_2^2 + T_1T_2 + T_1T_3 + \frac{1}{3!}T_1^3 + \frac{1}{2}T_1^2T_2 + \frac{1}{4!}T_1^4 \qquad \text{(II-7)}$$

Sample test runs have been made on H_2O and H_4 using all of the above terms.

2. Coupled cluster method (based on multireference determinants)

Since both our preliminary and large scale ab-initio configuration interaction calculations on CH_3NO_2 indicated a 2-configuration ground state, even at equilibrium geometry, and even more configurations along the C-NO_2 dissociation pathway, it has been apparent to us that multireference determinants would be necessary for coupled cluster or many-body perturbation theory calculations on nitro compounds.

We thus initiated as a first step the derivation of necessary formal equations for coupled cluster theory based on multireference determinants using

$$T = T_1 + T_2 \qquad \text{(II-8)}$$

$$e^{\hat{T}} = 1 + (T_1 + T_2) + \frac{1}{2}T_1^2 + \frac{1}{2}T_2^2 + T_1T_2 \qquad \text{(II-9)}$$

The basic premise was that the multireference determinants themselves already contained a sizable contribution from the important excitations. This is especially true for the way we obtain our multireference determinant which is from ab-initio configuration interaction calculations which are themselves based on multireference single and double excitations from the important multireference determinants from a smaller preliminary CI calculation.

The equations were derived at the Johns Hopkins University by Professor Laforgue and the method as defined by equation (II-9) has been coded by Dr. Roszak, debugged and is now undergoing testing.

3. Coupled cluster method (repetitive)

For a repetitive couple cluster method, e^{T} (using only lower T_j's) would be applied repetively to get terms to any desired degree of excitation. The advantage of such a repetitive method is that for higher orders of excitation one does not expand the number of equations that have to be soved at the same time.

As the first step in implementing this procedure, the equations were derived (by Professor Laforgue at the Johns Hopkins University) using

$$T = T_1 + T_2 \qquad \text{(II-10)}$$

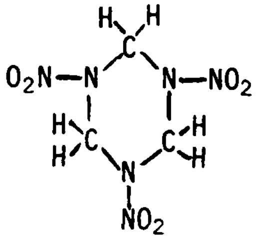
$$e^{\hat{T}} = 1 + (T_1 + T_2) + \frac{1}{2}T_1^{2} + \frac{1}{2}T_2^{2} + T_1T_2 \qquad \text{(II-11)}$$

as above.

This repetitive method as defined by equation (II-11) has been coded by Dr. Roszak for a single reference configuration, debugged and is now undergoing testing. The repetitive method is now also being extended to multireference determinants.

C. RDX preliminary results

The coupled cluster method has been applied to RDX



with two different choices of starting orbitals: localized and conventional canonical delocalized molecular orbitals.

1. Localized orbitals

For preliminary testing purposes, the canonical orbitals from an ab-initio MODPOT/VRDDO calculation (66 basis functions, 66 molecular orbitals of which 44 were occupied closed shell molecular orbitals) were localized following the criterion of Bays. From the 66 space orbitals (132 spin orbitals), a subset of 14 spin orbitals, of which eight were occupied, was selected. These occupied orbitals were localized mainly in the N-N region. From this set of orbitals 24 unique monoexcited (T_1), 216 diexcited configurations (T_2), 912 triexcited (T_3) and 1872 (T_4) configurations can be generated.

Even using just the linear approximations, the number of simultaneous equations to be solved using only

$$e^{T_1+T_2} \qquad \text{(II-12)}$$

$$N_1 = 24;\ N_2 = 216;\ N_1 + N_2 = 240$$

$$(N_1 + N_2)(N_1 + N_2) = 57600 = (240)^2 \qquad \text{(II-13)}$$

is 57,600, which is the total number of elements in the matrix.

The number of simultaneous equations to be solved using

$$e^{T_1+T_2+T_3+T_4} \qquad \text{(II-14)}$$

$$N_1 = 24;\ N_2 = 216;\ N_3 = 912;\ N_4 = 1872$$

$$(N_1 + N_2 + N_3 + N_4) = 3024$$

$$(N_1 + N_2 + N_3 + N_4) = 9,144,576 \qquad \text{(II-15)}$$

is 9,144,576.

Within the computer capacity of the computer on which these calculations are being run currently (fixed core with no virtual paging and an operating limit of no more than 131072 (= 2^{17}) words in any one array), it was not logistically feasible to solve 9,144,576 simultaneous non-linear equations. We analyzed the problem and a program written to solve a system of equations of that size, which would have to go in and out of computer core memory and would be a factor of the order of 50 times slower than an in-core program.

Thus, for the purposes of this preliminary testing, we used the linear approximations

$$e^{\hat{T}} = 1 + T_1 + T_2.$$

Solutions to the following two formulations were obtained:

a. Single reference function
$E_{corr} = -0.0105592$ a.u.

b. Repetitive correlation approach
$E_{corr} = -0.010600$ a.u.

[It is known that the linear coupled cluster approach may overestimate the correlation energy and use of this particular linear coupled cluster approach for the single reference was just for comparison purposes to the repeated correlation approach.]

The repetitive method is being derived and coded at present for multireference determinant functions.

2. Canonical orbitals

A large scale ab-initio CI calculation (using multireference determinants) had been run on an RDX using the same ab-initio MODPOT/VRDDO SCF calculation as in part a. Fourteen space orbitals had been used for that CI calculation (eight of which were occupied, and all of which had appreciable density in the N-N region) allowing all single and double excitations from the multireference determinants picked from a preliminary smaller CI calculation.

The two dominant configurations results from that multireference CI calculation were used as the multireference determinant function for this coupled cluster calculation.

Again the choice made for these coupled cluster calculations was the use of fourteen (14) molecular spin orbitals, eight (8) of which were occupied. These spin orbitals had appreciable density in the N-N region. Again, for the purposes of this preliminary testing we used the linear approximation

$$e^{\hat{T}} = 1 + T_1 + T_2$$

a. Single reference function:
$E_{corr} = -0.0285416$ a.u.

(Since the canonical orbitals used here were not localized as in part a. but only had appreciable density in the N-N region the coupled cluster correlation energy is somewhat larger than in part a. where the same coupled cluster correlation operator and a single reference function were used).

b. Multiconfiguration reference (ground state + one diexcited configuration - the only significant terms in the CI wave function).

$E_{corr} = -0.02854153$ a.u.

Note: In this case, part of the E_{corr} is absorbed into the multiconfiguration SCF energy.

We are planning to rerun the ab-initio CI calculations using localized orbitals by the Boys criterion. We will then carry out coupled cluster calculations on the CI multireference determinant wave function. This will enable a comparison of single reference and multireference coupled cluster based on localized orbitals and also a comparable comparison between single reference and repetitive coupled cluster based on either localized or delocalized molecular orbitals.

D. Further Investigations

We will be carrying out extensive testing of the repetitive approach and the multireference determinant approach to coupled cluster theory, and comparison of these to the results arising from testing including the various terms in the conventional coupled cluster approach. The objective is to develop a tractable desirable computational alternative to the brute force generation and solving of the rapidly ballooning of millions upon millions of simultaneous equations to be solved as the systems of interest become larger and larger.

III. Ab-initio quantum chemical calculations and electrostatic molecular potential contour maps for cationic polymerization

We have continued optimizing geometries and generating electrostatic molecular potential contour (EMPC) maps for new monomers of interest experimentally. Our previous results had illustrated vividly that these EMPC maps were capable of predicting reliably the basicity of even hypothetical monomers prior to their synthesis. The initiation step in the cationic polymerization of cyclic ethers is governed by the basicity of these monomers and our EMPC maps predicted reliably the rank order of polymerization and even optimal copolymer candidates.

A. Three-dimensional electrostatic molecular potential contour (EMPC) maps and image matching

We have also been working to develop methodology for more quantitative predictions of relative polymerization ratios. This is complicated by the fact that there are two steps in the polymerization: initiation--proportional to basicity and propagation--considered by experimental polymer chemists to be influenced by the electrophilicity of the propagating ring opened carbocation. We had already shown that these two steps are influenced in opposite and competing directions by the character of the substituent groups. We had also shown that initiation was a dominant step. Thus we have developed and implemented methods to calculate the volume, shape and accessibility of isopotential EMPC contours. We are now carrying out such calculations to compare against experimental data. We are also developing a strategy for comparing electrophilicities for the propagation step.

A further objective in this area of the research is to develop and test methods to predict quantitatively relative polymerization ratios. This is complicated because experimentally measured relative polymerization ratios are governed both by the initiation step (influenced by the basicity of the cyclic ether as exemplified by its EMPC maps and supplementarily by the steric accessibility for cationic attack at the oxygen) and by the electrophilicity of the propagating carbocation.

As the first step we are calculating the volume, shape and accessibility of some of the prototype exotic energetically substituted oxetanes such as oxetane, 3-fluoro-3-nitrooxetane and 3,3-dinitrooxetane. The relative volumes and other quantities are being calculated within various specified EMPC isopotential contours since this is a totally new theoretical approach and there may be depending on particular values of EMPC contours.

1. Methodology

An electrostatic molecular potential contour map is the set of points

$$V(\vec{r}) = -\int \frac{\rho(\vec{r}\,')d\vec{r}\,'}{|\vec{r}-\vec{r}\,'|} + \sum_{\alpha} \frac{Z_{\alpha}}{|\vec{r}-\vec{R}_{\alpha}|}$$

where $\rho(\vec{r}\,')$ is the electron density at $\vec{r}\,'$ (obtained from our ab-initio MODPOT/VRDDO/MERGE SCF programs), Z_{α} is the charge on nucleus α. For a typical molecule, $V(\vec{r})$ is calculated for about 30,000 different values of $\vec{r}$ distributed over a uniform three-dimensional grid. $V(\vec{r})$ is the potential a positive test charge experiences at $\vec{r}$. Thus, negative values of $V(\vec{r})$ indicate electrophilic regions, and positive values show nucleophilic regions. We will be calculating these quantities for a number of the other substituted oxetanes.

We are limited in the experimental data for relative polymerization ratios against which to compare. We will be carrying out such calculations for the oxetanes for which the experiments have been run.

There are several different approaches for computer image matching of EMPC maps for quantitative (or semi-quantitative) prediction of relative polymerization ratios.

a. Volume

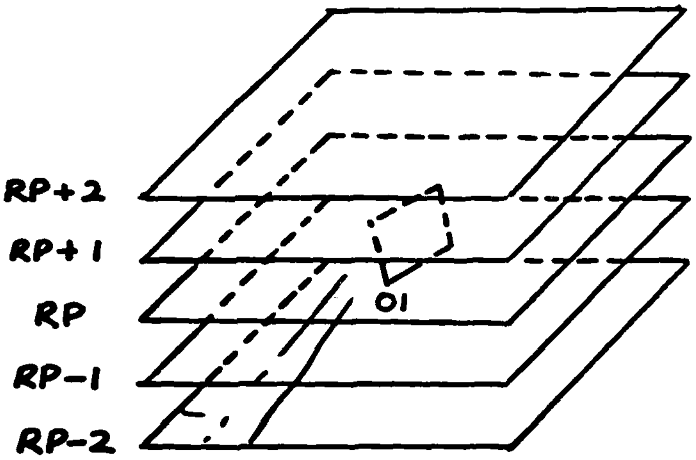
Match the volumes for various isopotential EMPC contours of differently substituted oxetanes.

b. Shape

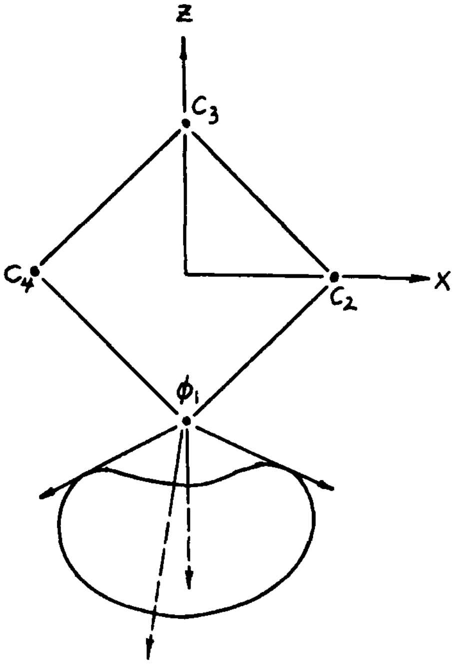
Compare the radii at which various isopotential EMPC contours of differently substituted oxetanes intersect a common set of vectors directed outward from designated points on the molecule (for example, fron the ring oxygen atom).

c. Accessibility

The regions of clear access to the various EMPC contours around the ring oxygen atom without interference from other parts of the molecule.

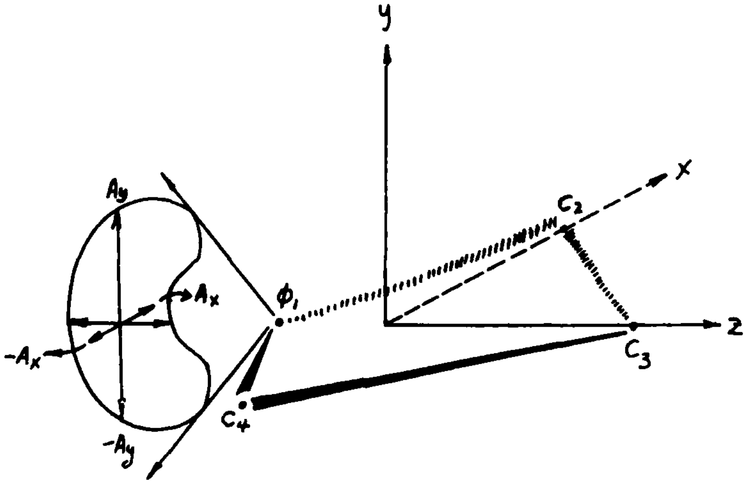


EMPC points are generated in a rectangular grid spanning each plane. The location and the number of the planes should be such as to give a complete, closed picture of the contour of interest (else the contour will be "clipped").



(1). Determine volume of a typical contour, say -20 Kcal/mole.

(2). Draw the vectors indicated, at least two in each coordinate plane. These are tangents from a selected point (ø1, in the example) to the contours.



(3). This set is a descriptor of the contour under consideration. It is possible to augment this descriptor set by additional vectors

2. Preliminary Results

a. Volume

The following results indicate that while the volume of the -20 kcal contour OXET > FNOX > DNOX, the averaged coordinates of the centroids of volumes are not very different.

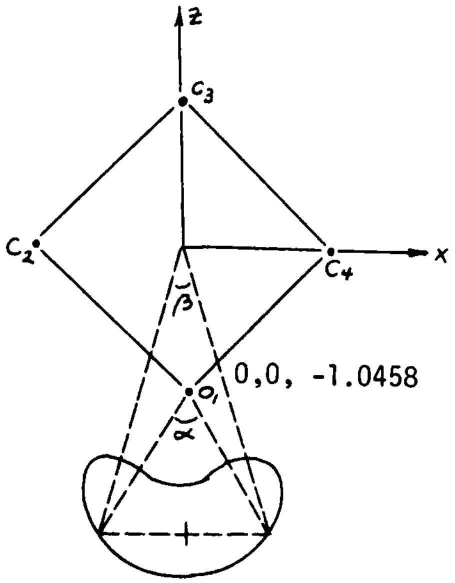
VOLUME OF -20 KCAL/MOLE CONTOUR

OXET	21.90	Å^3
FNOX	3.54	Å^3
DNOX	1.26	Å^3

AVERAGED COORDINATES OF THE VOLUME

OXET	0, 0, -2.37
FNOX	0, 0.01, -2.17
DNOX	0, 0, -2.17

Thus another approach was tried; namely, a measure of the shape and accessibility of EMPC isopotential contours.



	α_x	β_x	α_y	β_y
OXET	113.71	72.27	125.52	89.23
FNOX	80.62	46.21	106.93	66.63
DNOX	44.81	23.40	92.78	55.07

These results were a more clear indication of the relative probabilities for cationic attack on the oxetane oxygen than the coordinates of the centroid of the volume.

B. Molecules Calculated

We are still carrying out ab-initio MODPOT/VRDDO/MERGE calculations for geometry optimizations and generating EMPC maps for others of the large number of new substituted oxetanes of interest for cationic polymerization which Jerry Manzer had discussed with us on his visit to us at the Johns Hopkins University.

What makes the quantum chemical calculations so involved for most of the molecules Manzer mentioned is the number of multiple maxima and minima for their energies as a function of geometry.

Since so many geometries have to be calculated for these molecules, minor differences in integral prescreening and cut-off values became significant. We carried out extensive calculations with different integral threshholds and have established the appropriate criteria.

Many of the molecules are difficultly convergent in the SCF procedures. This difficult convergence had also affected our previous calculations on the calculations for proton attack on the cyclic ethers. We implemented new SCF routines with special convergence enhancing procedures which have overcome this problem.

We have carried out further calculations with these above improvements on a number of the cyclic ethers we previously investigated to assess the importance of such techniques. These results will be incorporated into the technical manuscripts which are being written or prepared.

Several manuscripts have been published. In our presentations at meetings we display the three-dimensional EMPC maps in a combination of various colors which give a vivid portrayal. It is difficult to portray three-dimensional EMPC maps in black and white for publication. The only feasible way to portray these in black and white is to display each three-dimensional EMPC isopotential contour seperately, which is less than desirable. We have been talking to publishers of several leading journals who have expressed possible interest in looking into publishing our EMPC maps in color provided we can provide appropriate color separates and providing their costs for such color pages is not too excessive.

During the past year, presentations of this research have been given at a number of national and international meetings and at other universities and research institutions.

At the invitation of Dr. Eli Pearce, Chairman of the 1983 Gordon Conference on Polymers, Dr. Kaufman presented the results of our research on quantum chemical investigations of the mechanism of cationic polymerization at that Gordon Conference, "Quantum Chemical Calculations on the Mechanism of Cationic Polymerization," July 1983. Our theoretical research is considered to be both pioneering and of forefront significance in the area of polymerization. There was a great deal of interest expressed from a number of industrial companies who manufacture polymers.

By invitation, Dr. Kaufman also presented an invited plenary lecture on the results on polymers, "Ab-Initio MODPOT/VRDDO/MERGE Calculations (Intra- and Intermolecular) for Polymers and Solids," at the NATO Advanced Study Institute on Quantum Chemistry of Polymers: Solid State Aspects, Braunlage/Herz, West Germany, July 1983.

By invitation, Dr. Kaufman also presented these results:
"Three-Dimensional Electrostatic Molecular Potential Contour Maps
A. Stereoelectronic Requisites for Biomedical Molecules
B. Cationic Polymerization," 8th Canadian International Theoretical Chemistry Symposium, Halifax, Canada, August 1983

Dr. Kaufman will also be presenting these polymer results at the BF Goodrich Company in October 1983.

Credit for the calculations on the polymers and the computer image matching is due to Dr. P. C. Hariharan.

IV. Prediction of Crystal Density

A. Background

Detonation pressures and detonation velocities are influenced by crystal densities.

To be able to predict crystal densities even for completely hypothetical compounds is of interest to ONR. While there are empirical methods to predict crystal densities, these methods depend only on the number and type of fragments or groups. These empirical methods are incapable of predicting differences in crystal densities between various position isomers of the same molecule. These empirical methods for crystal densities are also utterly incapable of predicting crystal structure arrangements.

Thus, we embarked several years ago on a project to calculate optimal crystal packing and crystal structure parameters based on potential functions from energy partitioned ab-initio intermolecular SCF calculations plus calculations of dispersion energy contributions.

Our approach aimed at evaluating the intermolecular interactions is based on nonempirical ab-initio calculations for smaller molecular aggregates (monomers, dimers, trimers, etc.), partitioning the total SCF interaction energies into the different components and then fitting these components individually to functional forms or, when necessary, recalculating or estimating explicitly for certain interaction components for each different unit cell dimension change plus calculated estimates of dispersion energy.

The general method was described in detail in our 1982 Annual Report on this project.

The main components of the two-body interaction energy are

$$\Delta E = E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND}^{(2)} + E_{DISP}^{(2)} \qquad (IV-1)$$

The first three contributions to equation IV-1 can be obtained from the decomposition of the variational E_{SCF} interaction energy corrected for basis set superposition error (BSSE).

$$\Delta E_{SCF} = E_{AB} - E_{A(B)} - E_{B(A)}$$

$$\cong \quad E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND,LE}^{(R)} + E_{IND,CT}^{(R)}$$

where

E_{AB}, $E_{A(B)}$, $E_{B(A)}$, denote the SCF total energies of interacting dimer, isolated monomers A and B (evaluated in the dimer basis set) respectively and where

$E_{EL}^{(1)}$ - the electrostatic contribution is further partitioned

$$= E_{EL,MTP}^{(1)} + E_{EL,PEN}^{(1)}$$

$E^{(1)}_{EX}$ - the exchange contribution

$E^{(2)}_{IND}$ - the induction contribution is further partitioned

$= E^{(2)}_{IND,LE} + E^{(2)}_{IND,CT}$

$E^{(2)}_{DISP}$ - the dispersion energy contribution.

In addition, the induction component contains also remaining (R) higher order correction (R) and it is decomposed into an additive long range classical component $E^{(R)}_{IND,LE}$ arising from interaction of local excitations (LE) with static charge distributions of other molecules and a short range $E^{(R)}_{IND,CT}$ corresponding to interaction of ionic charge-transfer configurations (CT) with static charge distributions.

B. Developments this Past Year

1. Programs

a. MOLASYS-INTER

(1). Calculation of atomic quadrupoles for use in calculating $E^{(1)}_{EL,MTP}$ and in calculating the electric field has been implemented, tested and used;

(2). An efficient initial guess has been added (which amelioates previous problems with non-convergence for some systems);

(3). Classical perturbation and variation perturbation expressions for calculating dispersion energy have been implemented and tested.

b. CRYSTAL

(1). Use of atomic quadrupoles in calculating $E^{(1)}_{EL,MTP}$ has been implemented, tested and used;

(2). Calculation of the electric field up through quadrupole terms at the molecules in the reference cell from all molecules in all surrounding unit cells has been implemented, tested and used;

(3). Calculation of two-body and three-body induction terms from the calculated electric field and atomic polarizabilities has been implemented, tested and used;

(4). Stepwise increase of crystal cluster size has been implemented and tested in order to investigate the convergence of the results with the increase of crystal cluster size.

2. Ab-Initio atom class-atom class potentials

a. Nature of anisotropy of non-empirical ab-initio atom-atom potentials

Most of the currently employed intermolecular atom-atom potential functions (either empirical or theoretical) are assumed to be isotropic, and very little is known about the nature of their anistropy on an atomic level. This situation strony limits the applicability of available potentials for studying properties of condensed matter, etc.

Based on our ab-initio interaction energy components calculated for the model CO dimer, we analyzed the nature of the anistropic contribution expressed in the form of atom-atom potentials. For this purpose, all the main contributions of the intermolecular interaction energy have been represented in the form of atom-atom $Q(\alpha)\ R_{00}^{-12}$ potentials for different angular orientations (α) of the CO dimer. (While the R_{00}^{-12} form is not optimal for all components, this gives us a chance to compare directly the anisotropy of all contributions simultaneously.) Results (Figure 1.) indicate that the observed anisotropy, i.e., α dependences of Q, is almost entirely due to the electrostatic multipole terms, whereas the exchange, electrostatic penetration, induction and dispersion contributions could be successfully represented by isotropic atom-atom potentials.

This reinforces our approach where we calculate the strongly anisotropic electric multipole terms, $E_{EL,MTP}^{(1)}$, directly from the cumulative atomic multipole moments derived from the molecular wave function.

The other terms $E_{EL,PEA}^{(1)}$, $E_{EX}^{(1)}$, and $E_{END,CT}^{(2)}$, we fit by the following isotropic potential

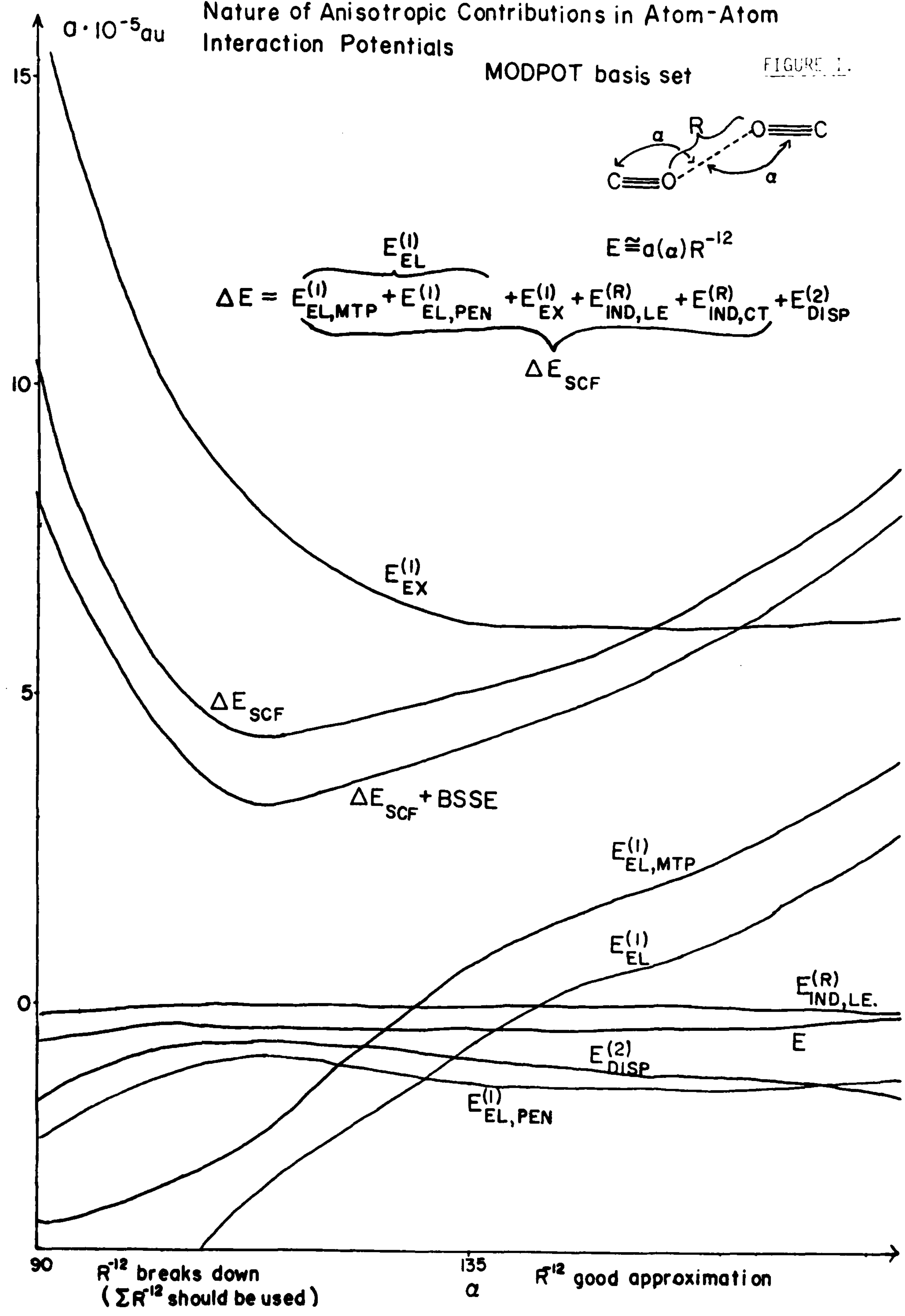
$$E = (\beta + \gamma R^{-1})\exp(-\delta R)$$

Besides the electrostatic multipole term, the next most anisotropic contribution seems to be dispersion interaction, but to a much smaller degree. This term is better fitted by $Q_6(\alpha)\ R_{00}^{-6}$ potential where Q_6 also displays some α dependence.

Nature of Anisotropic Contributions in Atom-Atom Interaction Potentials

MODPOT basis set

FIGURE 1.



b. Non-empirical atom-atom potentials for main components of intermolecular interaction energies

The aim of this research was to obtain non-empirical atom-atom potentials for each main term of intermolecular interaction energies by separately fitting ab-initio SCF interaction energy partitioned energy components evaluated for a number of model dimers (symmetric or mixed) within our energy decomposition scheme corrected for basis set superposition error (BSSE). The calculations have been performed with well-balanced minimal valence 3^s3^p MODPOT basis sets with ab-initio effective core model potentials known to yield interaction energies very close to results obtained with extended basis sets at much less computer time. The non-transferable ($E^{(2)}_{IND,CT}$) and strongly anistropic ($E^{(1)}_{EL,MTP}$) have been calculated explicitly each time from the cumulative atomic multipole moments (CAMM), up through quadrupole terms, obtained directly from the monomer wave functions. The short range exchange ($E^{(1)}_{EX}$), charge transfer ($E^{(2)}_{IND,CT}$) and electrostatic penetration ($E^{(1)}_{EL,PEN}$), have been represented by simplified potentials in the form of $(\beta + \gamma R^{-1})\exp(-\delta R)$, fitting corresponding results for dimers (symmetric or mixed) formed by HF, H_2O, NH_3, CH_4, CO, CO_2. These particular molecules were chosen as the most appropriate from which to obtain potentials for the first row atoms (C,N,O,F) and H.

The polarizability type terms α_a and α_b used in calculation of the $E^{(2)}_{IND,LE}$ from the calculated value of the electric field and α were obtained by equating $E^{(2)}_{IND,LE}$ directly from the energy-partitioned SCF wave function to the expression for $E^{(2)AB}_{IND,LE}$ calculated using the value of the electric field calculated within the atomic multipole expansions.

$$E^{(2)\,AB}_{IND,LE} = -1/2\left[\sum_{a\varepsilon A} \alpha_a(\vec{E}_a^{B\to A})^2 + \sum_{b\varepsilon B} \alpha_b(\vec{E}_b^{A\to B})^2\right]$$

c. Transferability of short range potentials for nitro compounds

From a large number of intermolecular ab-initio SCF calculations on $(CH_3NO_2)_2$ we fitted the short range ab-initio atom class-atom class potentials for OO, OH, NO and HH contacts. Similarly, from a large number of intermolecular ab-initio SCF calculations on the nitrobenzene, $C_6H_5NO_2$, dimer we fitted ab-initio atom class-atom class potentials for the OO, OH, NO and HH contacts.

FIGURE 2.

TRANSFERABILITY OF ATOM-ATOM POTENTIALS

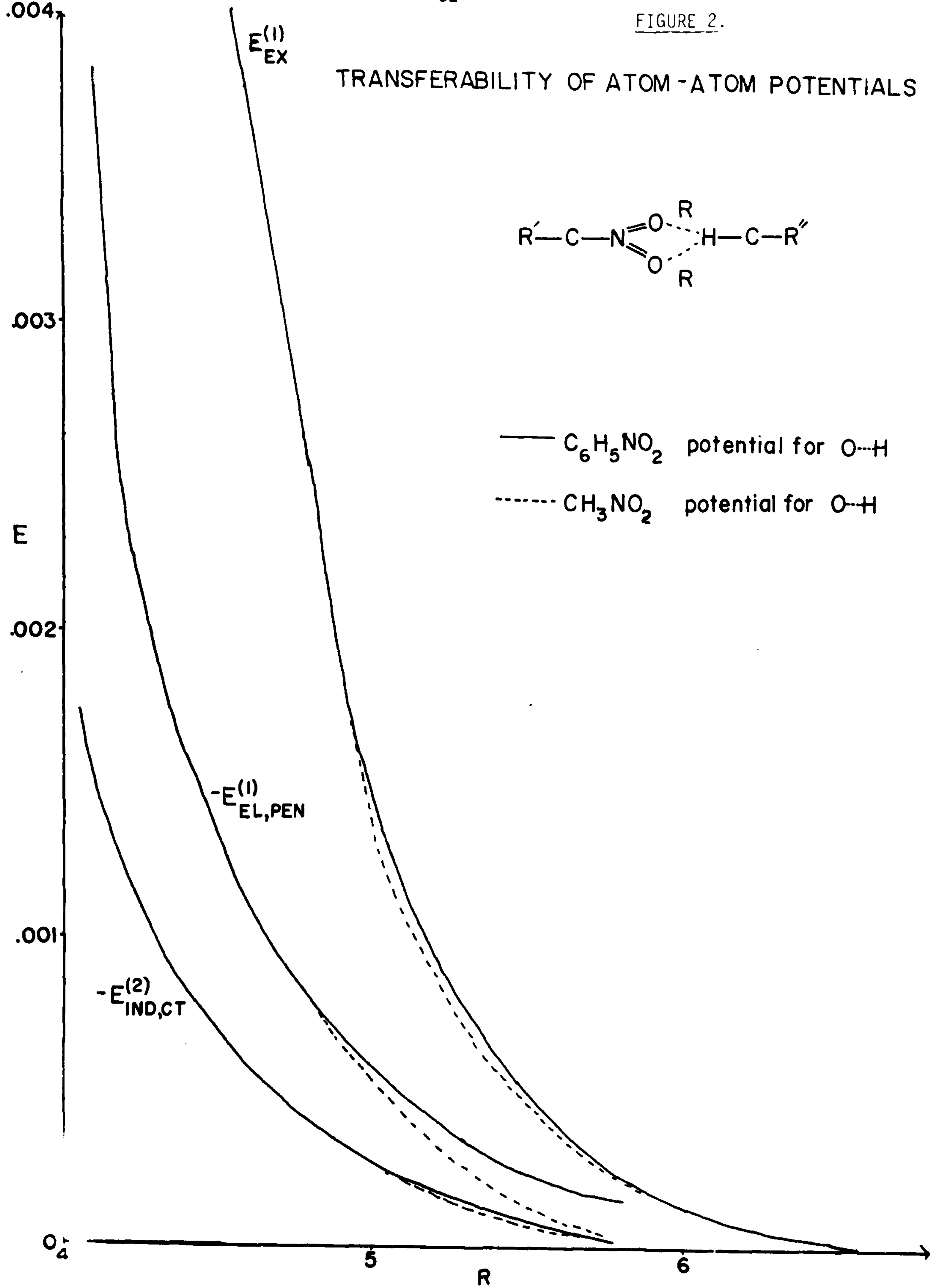
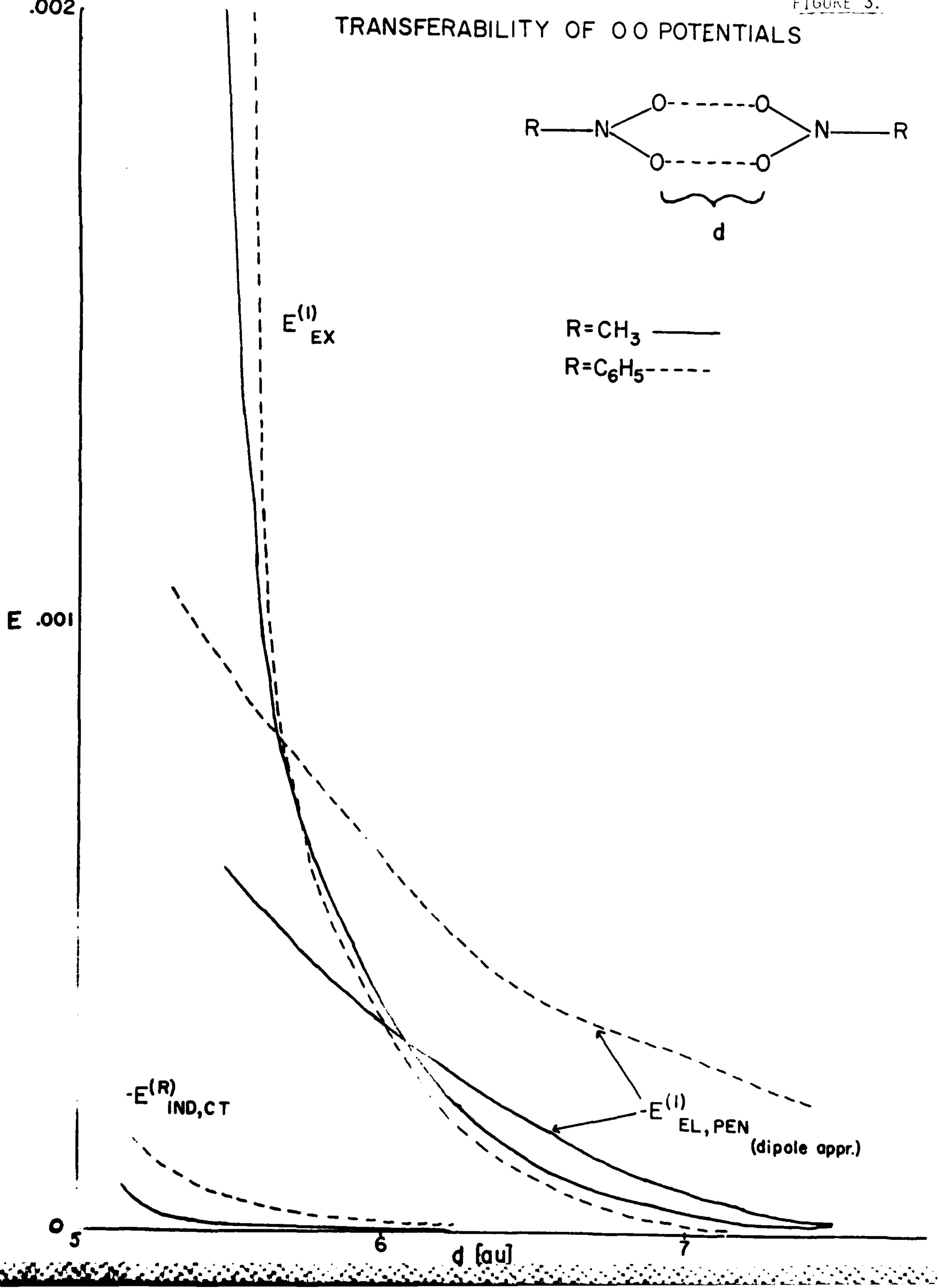


FIGURE 3.

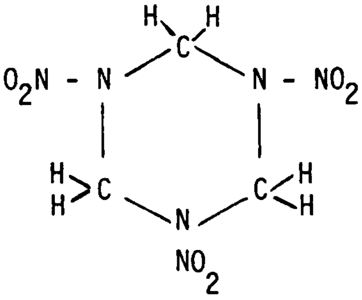


TRANSFERABILITY OF O O POTENTIALS

As can be seen from Figure 2, there is very close agreement in the fitted ab-initio short range O---H potentials $E_{EX}^{(1)}$, $E_{EL,PEN}^{(1)}$ and $E_{IND,CT}^{(2)}$ from CH_3NO_2 and from $C_6H_5NO_2$. As can be seen from Figure 3, there is also very close agreement in the fitted ab-initio short range O---O potentials $E_{EX}^{(1)}$ and $E_{IND,CT}^{(R)}$ from CH_3NO_2 and $C_6H_5NO_2$. There is a small absolute difference in the $E_{EL,PEN}^{(1)}$ potentials from CH_3NO_2 or $C_6H_5NO_2$; however, the curves are parallel. Also, the $E_{EL,PEN}^{(1)}$ term is small compared to the $E_{EL,MTP}^{(1)}$ term which is calculated explicitly for each intermolecular distance from the multipole expansion based on the SCF wave for the specific molecule.

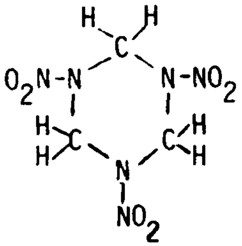
C. Results

Using the short range potentials fitted from ab-initio intermolecular calculations on the $(CH_3NO_2)_2$ dimer and explicit calculation of $E_{EL,MTP}^{(1)}$ and the electric field for calculation of $E_{IND,LE}^{(2)}$ from the ab-initio SCF calculation on RDX



we calculated the unit cell parameters of RDX to -1.0%(a), 1.5%(b), -0.6%(c) and the crystal density to 0.1% deviation from the experimentally measured crystal structure.

PREDICTED UNIT CELL PARAMETERS, VOLUMES AND CRYSTAL DENSITIES FROM AB-INITIO ENERGY PARTITIONED SCF CALCULATIONS

Crystal	Space Group	Number of Molecules in Unit Cell	Size of Cluster	Unit cell dimensions [Å] a	b	c	Unit Cell Volume [Å^3]	Crystal Density [g/cm^3]		Terms Included
CH_3NO_2	$P2_12_12_1$	4	∞	5.1832	6.2337	8.5181	275.31	1.471	exp	
	orthorhombic		46 (8Å radius)	5.4137	6.2357	8.5235	287.73	1.408	theor	All terms through quadupole level; short range potentials from $(CH_3NO_2)_2$ for OO, OH, NO, and HH contacts only; from 30 different molecular dimer pairs; 2- and 3-body induction interaction terms
			136 (12Å radius)	5.4057	6.2357	8.5241	288.33	1.410		Same as above; only 2-body induction interaction terms included.
				4.4 4.2	0.0 0.0	0.06 0.07	4.46 4.27	-4.46 -4.27	% dev	
RDX	Pbca	8	∞	13.182	11.574	10.709	1633.85	1.8056	exp.	
	orthorhombic		59 (12Å radius)	13.053	11.748	10.645	1632.83	1.8068	theor.	All terms through quadrupole level; short range potentials from $(CH_3NO_2)_2$ for OO, OH, NO and HH contacts only; α from 30 different molecular dimer pairs; only 2-body induction interaction terms included.
				-1.0	1.5	-0.6	-0.1	0.1	% dev.	

Major credit is due to Dr. W. Andrzej Sokalski for the improvements to the CRYSTAL program and the potentials. Credit is also due to Dr. Alfred H. Lowrey, Naval Research Laboratory, who is working with us collaboratively on the project as a fellow-by-courtesy of the Johns Hopkins University. Dr. Szczepan Roszak and Dr. John M. Blaisdell also contributed to this project.

V. Ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes

We have continued to carry out ab-initio calculations on polynitropolyhedranes and polynitropolyazapolyhedranes. The calculated quantum chemical indices such as total overlap populations (TOP's) between atoms (skeletal and skeletal-NO_2) as a function of nitration indicate whether and where nitration affects inherent bond strengths. Also, from these wave function we have been generating electrostatic molecular potential contour (EMPC) maps around these polynitropolyhedranes and polynitropolyazapolyhedranes. These EMPC maps appear to indicate that the character of the nitro groups may change as a function of the degree of nitration. Also these EMPC maps may prove useful in understanding how these molecules will pack in crystals.

Molecules which have a number of nitro groups around their peripheries could scarcely be expected to approach each other closer than a zero isopotential contour if the signs of the EMPC contour of the adjoining molecules are the same. On the other hand, if the molecules are surrounded by by molecules with both positive and negative EMPC contours, the molecules may try to orient themselves in a crystal having regions of positive EMPC contours around one molecule adjoining regions of negative EMPC contours around the other molecule.

A. Electrostatic molecular potential contour (EMPC) maps around nitrocubanes

As an indication that the character of the nitro groups might be changing as a function of the degree of nitration, the EMPC maps for 1,3,5,7-tetranitrocubane and for octanitrocubane are presented on the next pages (Figures 4 and 5).

The small, very dark 2,000 kcal/mole isopotential contours are "black" and denote the positions of the nuclei. The next darker -10 kcal/mole isopotential contours are located around the nitro groups. However, in the 1,3,5,7-tetranitrocubane, these -10 kcal/mole EMPC regions are rather delocalized around the entire NO_2 group. In octanitrocubane (which is in exactly the same orientation as the 1,3,5,7-tetranitrocubane), the -10 kcal/mole contours in the regions of the NO_2 groups are much more sharply localized over the individual atoms.

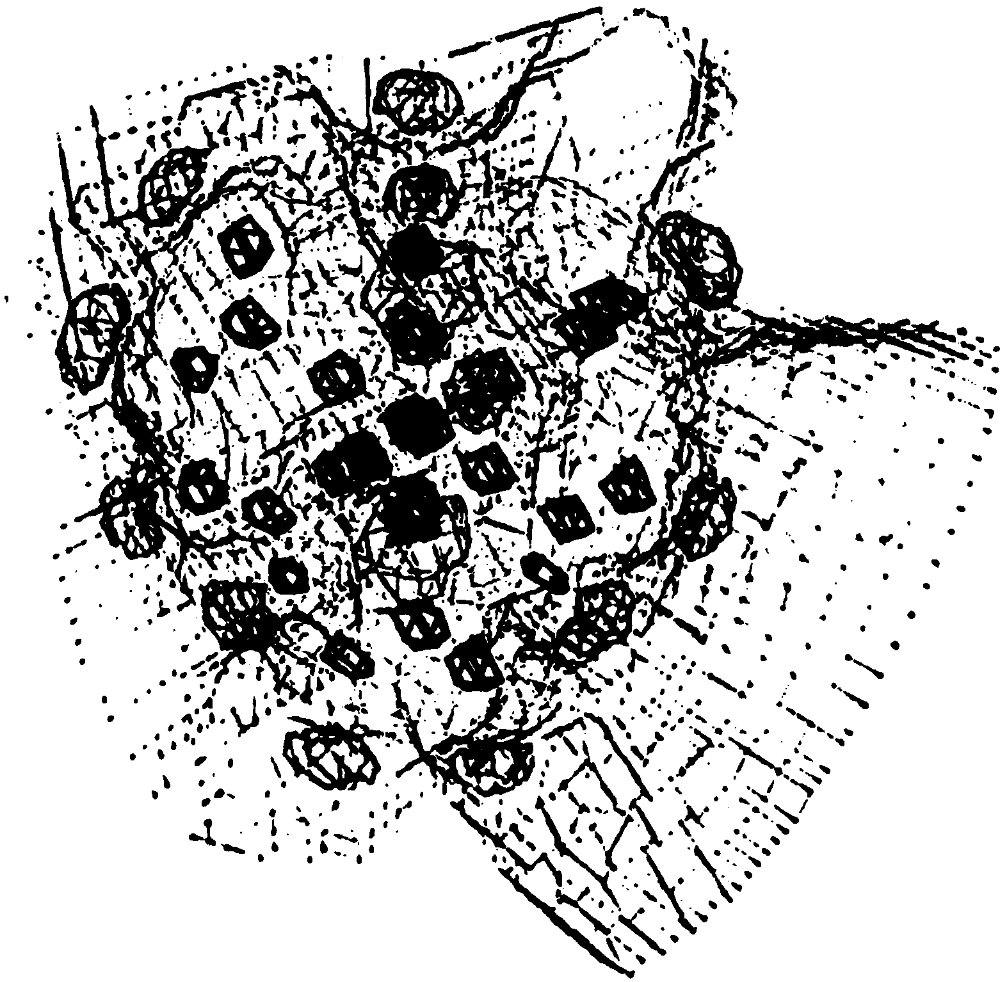
B. Polynitroadamantanes

We have carried out ab-initio MODPOT/VRDDO calculations on other polynitroadamantanes whose crystal structure had been determined experimentally, and also from these calculated wave functions generated the three-dimensional isopotential EMPC maps.

Among the compounds investigated were tetranitroadamantane and gens-dinitroadamantane.

This will give us some feeling for the magnitudes of various quantum indices for compounds that do exist.

Major credit for these calculations is due to Dr. P.C. Hariharan.



OCTANITROCUBANE

BLACK=2000.0 RED=20.0
BLUE=-10.0 KCAL/MOLE

FIGURE 4.

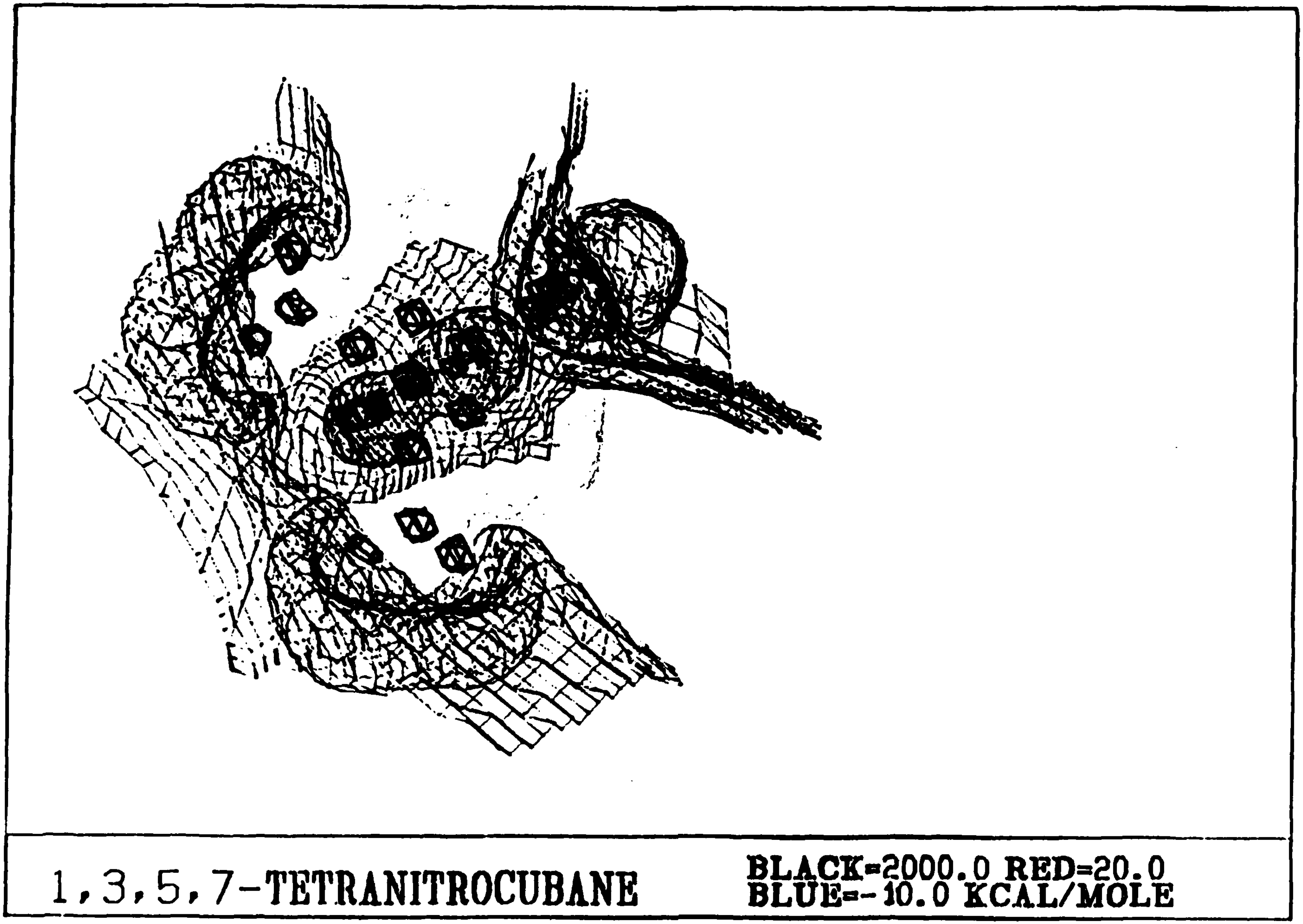

1,3,5,7-TETRANITROCUBANE
BLACK=2000.0 RED=20.0
BLUE=-10.0 KCAL/MOLE

FIGURE 5.

VI. Ab-initio configuration interaction calculations on the CH_3-NO_2 decomposition pathway of nitromethane

Ab-initio configuration interaction calculations using multireference determinants have been carried out for much of the CH_3-NO_2 decomposition pathway of nitromethane. For each point in the order of 800,000 configurations were generated. Using a perturbation procedure the energy contribution of each configuration was calculated. All configurations contributing to an energy higher than a chosen threshold were included in the CI wave function to be solved. Then an extrapolation was performed to take into account the energy contributions of the configurations not included explicitly. This was then followed by a Davidson type correction for size consistency.

A. Details of configuration interaction calculations

Reference configurations = 19 (All single and double excitations from these 19 reference configurations)

Electronic states explored = 4

Total SAF's generated = 845,020 (at equilibrium C-N distance 2.8 a.u.)

Interaction (selection) threshold = 0.000050 Hartree

r(C-N) a.u.	2.3	2.8	3.3	3.8	4.3	4.8
SAF's (selected)	4647	4449	4075	4780	4616	4715

E(CI): SAF's selected

E(extrapolated): Calculated from summation of energy lowerings for rejected SAF's at 2 or more thresholds.

$$E(\text{full CI}) = E(\text{ext.}) + \left(1 - \sum_{p}^{\text{ref.}} C_p^2\right) [E(\text{ext.}) - E(\text{ref})]$$

E(ref) ≡ Energy from only reference configurations.

B. Results

There are several significant aspects of these CI results on CH_3NO_2.

1. Multiconfigurational character even of ground electronic state at equilibrium geometry

First, even at the equilibrium geometry for the electronic ground state of CH_3NO_2 there is a significant multiconfiguration character. This is due to a double excitation localized out-of-plane on the NO_2 group.

As the r_{C-N} is increased, even additional configurations become important (corresponding to breaking the C-N σ bond) in addition to the multiconfigurational character localized on the NO_2 group which always remains important.

For the first excited and higher excited states, there is even more mixing and even stronger multiconfiguration character at each r_{C-N} distance.

Thus, even for the ground electronic state of CH_3NO_2 multireference determinants will be necessary for CI calculations or for many-body perturbation theory or for coupled cluster theory calculations.

2. The molecular orbital ordering of both occupied and virtual orbitals changes between 3.3 and 3.8 a.u.

We denote the orbitals described as

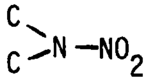
σ_{C-N}	bonding in the C-N bond in the plane of the NO_2 group
σ^*_{C-N}	antibonding in the C-N bond in the plane of the NO_2 group
$\pi_{O_1O_2}$	occupied, localized primarily on O_1O_2 perpendicular to the plane of the NO_2 group
$\pi^*_{NO_1O_2}$	unoccupied, localized primarily on NO_1O_2 perpendicular to the plane of the NO_2 group

	2nd HOMO	HOMO	LUMO	2nd LUMO
$\leq$ 3.3 a.u.	σ_{C-N}	$\pi_{O_1O_2}$	$\pi^*_{NO_1O_2}$	σ^*_{C-N}
$\geq$ 3.8 a.u.	$\pi_{O_1O_2}$	σ_{C-N}	σ^*_{C-N}	$\pi^*_{NO_1O_2}$

Major credit for these CI calculations is due to Dr. Cary Chabalowski.

VII. Ab-initio configuration interaction calculations on RDX

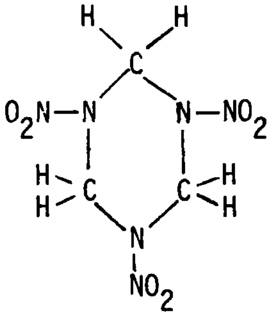
Preliminary CI calculations were carried out on RDX at equilibrium considering the molecular orbitals centered primarily on a



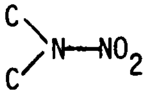
portion of the skeleton as a prototype for the N-NO_2 decomposition. Even at equilibrium a multireference determinant character on the NO_2 group was found--similar to that in CH_3NO_2. Thus, it appears to be a general characteristic of all aliphatic nitroexplosives.

A. Details of the calculation

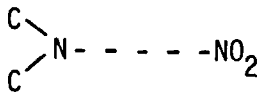
For this preliminary test CI calculation on RDX



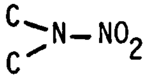
we used our customary ab-initio MODPOT basis set and the VRDDO prescreening option which cuts down considerably on the number of integrals to be calculated. There were 42 occupied molecular orbitals. Of these, 17 occupied molecular orbitals were retained as well as 15 virtual orbitals for the configuration interaction calculation. These molecular orbitals were ones with their dominant contributions in a particular one of the

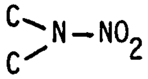


regions as a model for a



decomposition pathway. The ab-initio CI calculation was a multireference determinant calculation allowing all single and double excitations from 19 reference configurations. The total number of SAF's generated was 368,845. The energy contribution from each of these SAF's was estimated by a perturbation procedure and all SAF's contributing an energy more than a certain threshold were retained (3360 configurations) for the CI calculation. Four roots were obtained corresponding to the ground and first three excited singlet configurations. Then the energy contributions from the remaining configurations were added by extrapolating. Following that a Davidson type correction was added for size-consistency.

Even in the ground electronic state at the equilibrium geometry of RDX there were contributions from the doubly excited closed and open shell configurations localized on the NO_2 group as well as smaller contributions from other configurations in that  region.

A CI calculation on the RDX molecule taking into account simultaneously the three  regions would be expected to have similar contributions from all three groups simultaneously.

We will be investigating further CI calculations on the decomposition of RDX.

Major credit for these CI calculations is due to Dr. Cary Chabalowski with the collaboration of Dr. P.C. Hariharan.

VIII. Conversion of our programs to vector supercomputers, CYBER 205 and CRAY

The quantum chemical problems we are investigating involve large scale calculations on large systems, both with many atoms and/or with many configurations or simultaneous equations to be solved. We have gotten access to CYBER 205 time and to CRAY time. The CYBER 205 has two million 64 bit words in real memory plus virtual memory. The CRAY has one million 64 bit words of real memory. We are in the process of converting our programs to both of these machines.

We are enthusiastic about computing on these supercomputers because they will enable us to do many problems we are investigating in the ONR (and ARO) research which have been virtually intractable in more conventional computers.

However, these conversions of our programs to the CYBER 205 and to the CRAY are non-trivial even just to convert the programs to get them running even before vectorizing the programs for optimal speed since:

A. Our programs are large and to run them in conventional machines we had to make extensive use of moving data in and out of mass storage which is now only partly necessary and is done in a different manner on the CRAY and in a yet different manner on the CYBER 205.

B. Our programs made extensive use of masking and bit shift operations which are done in a different manner on the CRAY and in yet a different manner on the CYBER 205.

C. The permissible FORTRAN on the computers we have been running (CDC 6600, CDC 7600, CYBER 175) is somewhat different than the permissible FORTRAN on the CRAY and is somewhat different than the permissible FORTRAN on the CYBER 205. (The permissible FORTRAN on the CRAY and on the CYBER 205 are also different from one another.)

D. The CYBER 205 is a newer computer than the CRAY and hence its operating system is still undergoing developmental changes which sometimes necessitates changes in the program.

However, we have already sucessfully converted one of our programs and we are working on the others. We will then work on proper vectorization of the code for optimal running speed.

Major credit is due to Dr. P.C. Hariharan in this endeavor.

IX. Lectures Presented on this ONR Research (*denotes invited lecture)

A. Already Presented, October 1, 1982 - September 30, 1983
Dr. Joyce J. Kaufman

1. At National or International Meetings

* "Ab-Initio MODPOT/VRDDO/MERGE Intermolecular Calculations for Crystals," Sanibel International Symposium on Molecular and Solid State Theory and Computational Quantum Chemistry, Palm Coast, Florida, March 1983.

* "Ab-Initio MODPOT/VRDDO/MERGE SCF and Beyond Hartree-Fock Calculations on Energetic Compounds," Sanibel International Symposium on Molecular and Solid State Theory and Computational Quantum Chemistry, Palm Coast, Florida, March 1983.

"Ab-Initio MODPOT/VRDDO/MERGE Intermolecular Calculations to Derive Atom Class-Atom Class Potential Functions," American Physical Society Spring Meeting, Baltimore, Maryland, April 1983.

"Prediction of Crystal Densities Using Atom Class-Atom Class Potential Functions from Energy Partitioned Ab-Initio SCF Calculations," American Physical Society Spring Meeting, Baltimore, Maryland, April 1983.

* "Quantum Chemical Calculations on Mechanism of Cationic Polymerization," Gordon Conference on Polymers, New London, Conn., July 1983.

* "Ab-Initio MODPOT/VRDDO/MERGE Calculations (Intra- and Intermolecular) for Polymers and Solids," NATO Advanced Study Institute on Quantum Chemistry of Polymers: Solid State Aspects, Braunlage/Herz, West Germany, July 1983.

* "Prediction of Crystal Densities Using Ab-Initio Potential Functions from Energy-Partitioned Ab-Initio MODPOT/VRDDO Intermolecular SCF Calculations Plus Dispersion," 8th Canadian Theoretical Chemistry Symposium, Halifax, Canada August 1983.

* "Three-Dimensional Electrostatic Molecular Potential Contour Maps
A. Stereoelectronic Requisites for Biomedical Molecules
B. Cationic Polymerization," 8th Canadian International Theoretical Chemistry Symposium, Halifax, Canada, August 1983.

IX. Lectures Presented on this ONR Research (*denotes invited lecture)

A. Already Presented (cont.)

"Ab-Initio MODPOT/VRDDO/MERGE Intermolecular Calculations to Derive Atom Class-Atom Class Potential Functions," American Chemical Society Fall National Meeting, Washington, D.C., September 1983.

"Prediction of Crystal Densities Using Atom Class-Atom Class Potential Functions from Energy Partitioned Ab-Initio SCF Calculations," American Chemical Society Fall National Meeting, Washington, D.C., September 1983.

"Ab-Initio MODPOT/VRDDO/MERGE SCF Calculations on Energetic Compounds: Nitrocubanes," American Chemical Society Fall National Meeting, Washington, D.C., September 1983.

"Ab-Initio CI Calculations on CH_3NO_2 Confirm the Multiconfigurational Character of Both Ground and Electronically Excited States Even at Equilibrium Geometries," American Chemical Society Fall National Meeting, Washington, D.C., September 1983.

B. Invited Lectures Presented at ONR or DOD Meetings: Joyce J. Kaufman

"Ab-Initio Quantum Chemical Calculations on Large Polynitro-Polyhedranes; CI Calculations on the Dissociation Pathway of CH_3NO_2; Prediction of Crystal Densities, ONR Workshop to Review Dense Explosives Research Program and Opportunities, China Lake, California, April 1983.

"Quantitative Measurement from Electrostatic Molecular Potential Contour Maps of Oxetanes," Energetic Polymer Workshop, Great Oak, Maryland, July 1983. (Dr. P.C. Hariharan)

"Ab-Initio Calculations on Nitroexplosives and Prediction of Crystal Densities," Chemical Decomposition of Energetic Materials, Great Oak, Maryland, August 1983.

X. Papers Published on This ONR Research, October 1982 - September 1983

A. Already Published

1. W.A. Sokalski, S. Roszak, P.C. Hariharan and Joyce J. Kaufman, "An Improved SCF Interaction Energy Decomposition Scheme Corrected for Basis Set Superposition Effect," Int. J. Quantum Chem. 23, 847-854 (1983).

2. P.C. Hariharan, W.S. Koski, Joyce J. Kaufman and Richard S. Miller, "Ab-Initio MODPOT/VRDDO/MERGE Calculations on Energetic Compounds III. Nitroexplosives: Polyaminopolynitrobenzenes (Including DATB, TATB, and Tetryl),*" Int. J. Quantum Chem. 23, 1493-1504 (1983).

*Paper XVII in the Series "Molecular Calculations with the Non-Empirical Ab-Initio MODPOT/VRDDO/MERGE Procedures."

3. W. A. Sokalski, P.C. Hariharan, and Joyce J. Kaufman, "An SCF Interaction Energy Decomposition Study of 12 Hydrogen Bonded Dimers," J. Phys. Chem., 87, 2803 - 2810 (1983).

B. Accepted for Publication and In Press

1. W.A. Sokalski, P.C. Hariharan, and Joyce J. Kaufman, "Guidelines for Development of Basis Sets for First Order Intermolecular Energy Calculations," in press, J. Comp. Chem.

2. W.A. Sokalski, S. Roszak, P.C. Hariharan, Walter S. Koski, Joyce J. Kaufman, A.H. Lowrey and R.S. Miller, "Crystal Structure Studies Using Ab-Initio MODPOT/VRDDO SCF Energy Calculations. I. N_2 and CO_2 Test Cases. II. Nitromethane," an invited paper presented at the Sanibel International Symposium on Molecular and Solid State Theory and Computational Quantum Chemistry, Palm Coast, Florida, March 1983. In Press, Int. J. Quantum Chem., Symposium Issue.

3. P.C. Hariharan, Joyce J. Kaufman, Alfred H. Lowrey and Richard S. Miller, "Ab-Initio MODPOT/VRDDO/MERGE Calculations on Energetic Compounds. IV. Nitrocubanes: Mononitro- to Octanitro- Quantum Chemical Calculations and Electrostatic Molecular Potential Contour Maps," an invited paper presented at the Sanibel International Symposium on Molecular and Solid State Theory and Computational Quantum Chemistry, Palm Coast, Florida, March 1983. In press, Int. J. Qunatum Chem.

4. Joyce J. Kaufman, "Ab-Initio Potential Energy Functions for Scattering from Energy Partitioned Ab-Initio SCF Energies Plus Dispersion - Workshop Note," presented at the Sanibel International Symposium on Molecular Scattering and Quantum Chemistry, Palm Coast, Florida, March 1983. In press, Int. J. Quantum Chem., Symposium Issue.

X. Papers Published on This Research (cont.)

B. Papers Accepted for Publication and In Press (cont.)

5. Cary Chabalowski, P.C. Hariharan, Joyce J. Kaufman and Robert J. Buenker, "Ab-Initio Multireference CI Calculations on CH_3NO_2 Confirm Earlier Preliminary GVB and MCSCF/CI Results that HNO_2 and CH_3NO_2 Have Multiconfiguration Ground as Well as Electronically Excited States Even at Equilibrium Geometry, a Symposium Note," presented at the Sanibel International Symposium on Molecular and Solid State Theory and Computational Quantum Chemistry, Palm Coast, Florida, March 1983. In Press, Int. J. Quantum Chem., Symposium Issue.

XI. Project Personnel

The following scientific personnel worked full or part time with this present ONR project.

Joyce J. Kaufman, Ph.D., Principal Investigator

P. C. Hariharan, Ph.D., Associate Research Scientist

Overall responsibility for implementing new program developments.

Quantum chemical calculations on energetic polymers.

Quantum chemical calculations on the large nitroexplosives and polynitropolyhedranes.

Development of programs for graphical display of three dimensional isopotential electrostatic molecular potential contour maps for visual display and for computer image matching.

Cary Chabalowski, Ph.D., Associate Research Scientist

Program implementation of large scale ab-initio configuration interaction program based on multireference determinants.

Configuration interaction calculations on the C-NO_2 decomposition pathway of nitromethane.

Configuration interaction calculations on RDX.

Terminated September 15, 1983.

W. Andrezj Sokalski, Ph.D., Postdoctoral

Further development and implementation of program for partitioning of the SCF wave functions and energies into their various components and addition of higher order terms.

Carrying out SCF intermolecular calculations for additional test molecules for CRYSTAL calculations.

Implementing calculations of additional terms in CRYSTAL program itself.

CRYSTAL calculations on CH_3NO_2 and RDX.

Now carrying out CRYSTAL calculations for other systems.

Szczepan Roszak, Ph.D., Postdoctoral

Implemented program for many-body and coupled cluster multi-determinant repetitive calculations using both strictly orthogonalized localized molecular orbitals and conventional canonical delocalized molecular orbitals.

Coupled cluster test calculations.

Coupled cluster calculations on RDX.

John M. Blaisdell, Ph.D., Postdoctoral

Derived and implemented ab-initio crystal orbital program.

Fitted additional potential functions for molecules for CRYSTAL.

Terminated October 30, 1983.

Alexandre Laforgue, Ph.D., Visiting Scientinst

Derivation of new approach to many-body theory, multideterminant reference states and iterative calculations.

Terminated December 1982.

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