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NEW THEORETICAL CONCEPTS FOR UNDERSTANDING ORGANIC REACTIONS

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Suggested Computational Problems

NATO Advanced Study Institute

NEW THEORETICAL CONCEPTS FOR UNDERSTANDING ORGANIC REACTIONS

19th June - 2nd July 1988

Sant Feliu de Guíxols, Spain

STANDARDIZATION GROUP (UK)

FPO NY 09510 1570

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Tutors

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Problem 1

A number of conformational potential surfaces

$$E = E(x1,x2) \qquad (1)$$

and hypersurfaces,

$$E = E(x1,x2,x3) \qquad (2)$$

that have already been studied will be reinvestigated. Analytic functions of the form

$$E = Eo + \text{sum } ci.f1i(x1).f2i(x2) \qquad (3)$$

and

$$E = Eo + \text{sum } ci.f1i(x1).f2i(x2).f3i(x3) \qquad (4)$$

will be fitted to the previously generated SCF grid points for surfaces and hypersurfaces respectively. The results obtained by the students will be compared with published results.

For references about problems 1,2 and 3, see abstract L1 in the NATO ASI booklet.

Problem 2

Double rotors with 2 torsional angles: x1 and x2, associated with the systems of fully hydrogenated molecules of the type X-Z-Y will be subjected to conformational study. This study is analogous to those of PART I but the SCF energy grid points are expected to be evaluated within the school. Because of time limitations STO-3G basis set will be used in evaluating the SCF grid points and the molecular geometry will not necessarily be optimized. The least amount of problem expected when the central atom is carbon (Z=C) and X as well as Y may be C, N or O.

C-C-C	C-C-N	C-C-O
	N-C-N	N-C-O
		O-C-O

The simplest of these species is CH3-CH2-CH3 located at the upper left hand corner of the above hemi-matrix. The other two hemi-matrices with Z=N and Z=O have a similar set of fully hydrogenated compounds that may pose certain problems at the level of SCF convergence.

Problem 3

The generated and fitted potential energy surfaces will be subjected to topological analysis. First of all the first derivatives of equation (3) for surfaces and equation (4) for hypersurfaces will be evaluated and be set equal to zero in order to locate the whereabouts of the critical points. Subsequently, at the location of each of the critical points the second derivatives of E (from equations 3 and 4 for surfaces and hpersurfces respectively) will be evaluated in order to determine the order (L) of the critical points a surface may have. For a minimum L=0, and for a transition state L=1. The value of L=2 is a maximum for a surface and supersaddle point for a hypersurface. The maximum for a hypersurface has a characteristic L=3 value.

Conformational surfaces obey the following alternating sum rule for the number of critical points (NL), where L will run from o to n and n is the dimensionality of the problem. (For surfaces n=2 and hypersurfaces n=3)

$$\text{sum } [(-1)^{**}L]\ NL = 0 \qquad (5)$$

For an ideal surface

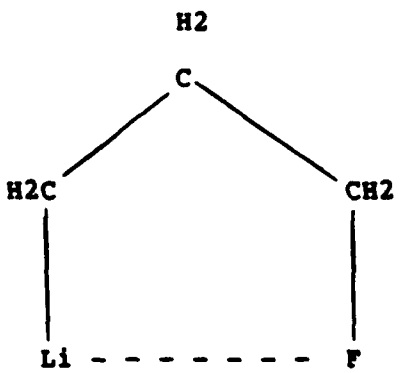
$$Nl = ml.m2.BL \qquad (6)$$

and for an ideal hypersurface

$$N1 = m1.m2.m3.BL \qquad (7)$$

where mi's represent the topological periodicity along each of the one dimensional location. BL is the Betti numbers which are the binomial coefficients (n over L) for conformational problems.

Certain chemical systems with too much repulsive or too much attractive interaction will not obey equations (6) or (7). Those who wish to explore such unique conformational situations might attempt to study the following molecule



with two torsional angles (x1 and x2) along the pair of C-C bonds. This disubstituted propane is expected to show a markedly different potential energy surface topology in comparison to that of unsubstituted propane.

Problem 4

HCN-HNC Rearrangement

The HCN -> HNC reaction has been used frequently to illustrate transition structure optimization methods. At the HF/STO-3G level, the reactant geometry is: R(CN)=1.153 A, R(CH)=1.070 A (linear); the product geometry is: R(CN)=1.170 A, R(NH)=1.011 A (linear). In this project with GAUSSIAN 86, you will use the linear synchronous transit(LST method to get near the transition state and gradient optimization methods to locate it exactly.

Suggested plan of attack:

(1) Starting from the reactants and products, use the linear synchronous transit method to locate the transition structure approximately.

(2) Calculate the gradient and frequency at the LST optimized structure. Is it a stationary point? Is it a saddle point?

(3) Optimize the transition structure using OPT=TS. Don't forget to have the program calculate a few critical force constants.

(4) Test the optimized transition state by calculating the frequencies.

References:

LST: Halgren and Lipcomb, CPL 49 pg 225 (1977)

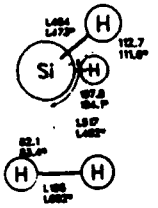
TS opt: Schlegel, Adv.Chem.Phys. 67 pg 249 (1987), J.Comp.Chem. 3 pg 214 (1982)

HCN ts: Ishida, Morokuma and Kormornicki: JCP 66 pg 2153 (1977)

Problem 5

SiH2 + H2 -> SiH4 Insertion Reaction

The ground state of SiH2 is a singlet with an sp2 lone pair. Like singlet carbene, SiH2 inserts readily into covalent bonds. The least motion pathway would proceed through a C2v symmetry transition state (sp2 lone pair pointing at the H2 sigma bond). However, this path is forbidden by orbital symmetry, and the reaction goes via a non-least motion pathway. The allowed transition state has Cs symmetry with the sp2 lone pair of SiH2 nearly parallel to H2.



The geometry of the reactants is R(SiH)=1.531 A, <HSiH=93.8 R(H2)=0.735 A; for the product R(SiH)=1.487 (all data at HF/3-21G). The transition state has a 50 percent elongation of the H2 bond. In this project, GAUSSIAN 86 will be used to determine the transition state at the HF/3-21G level.

Suggested plan of attack:

(1) Construct several different Z-matrix coordinate systems for the transition state. Choose the best coordinate system for the rest of the calculations.

(2) Calculate the energy and gradients at several points along an approximate reaction path to get a rough location of the transition state.

(3) Optimize the transition structure using gradients. Start with an analytically calculated Hessian (the CALCFC option).

(4) Test the transition state by calculating the vibrational frequencies. Sketch the transition vector and the transition structure.

(5) Draw an orbital interaction diagram for the transition state and discuss why the non-least motion pathway is allowed but the least motion pathway is forbidden.

References:

Fleming: Frontier Orbitals and Organic Chemical Reactions.

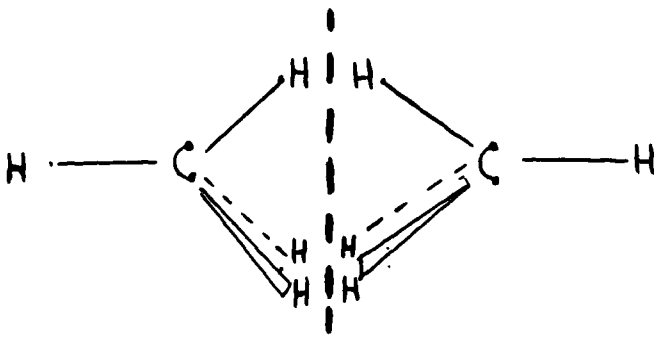
Colvin, Grev, Schaefer and Bicerano: CPL 99 pg 399 (1983)

Sosa and Schlegel: JACS 106 pg 5847 (1984)

Problem 6

Planar tetracoordinated carbon and the inversion of CH4

The possibility of planar tetracoordinated carbon has long fascinated theoretical and experimental chemists. The simplest hydrocarbon, CH4 (Td symmetry), can be distorted planar (D4h symmetry). Planar methane is a potential transition state for the inversion of configuration of tetrahedral methane to give its mirror image.



In this project, GAUSSIAN 86 will be used to explore the potential energy surface of methane at the HF/3-21G level. The aim of the exercise is to illustrate higher order saddle points and how to get to lower order saddle points, and eventually to the transition state (first order saddle point).

Suggested plan of attack.

(1) Optimize tetrahedral methane.

(2) Optimize planar methane (D4h) and calculate the frequencies. Is it a transition state (first order saddle point)?

(3) Displace the structure along any one of the normal modes with an imaginary frequency (except for the mode that leads to the Td minimum).

(4) Optimize the distorted structure and calculate the frequencies. If it is not a first order saddle point, go back to (3).

(5) Make a sketch of the methane potential energy surface indicating the energetics and connectivity of the minima and the various first and higher order saddle points.

References.

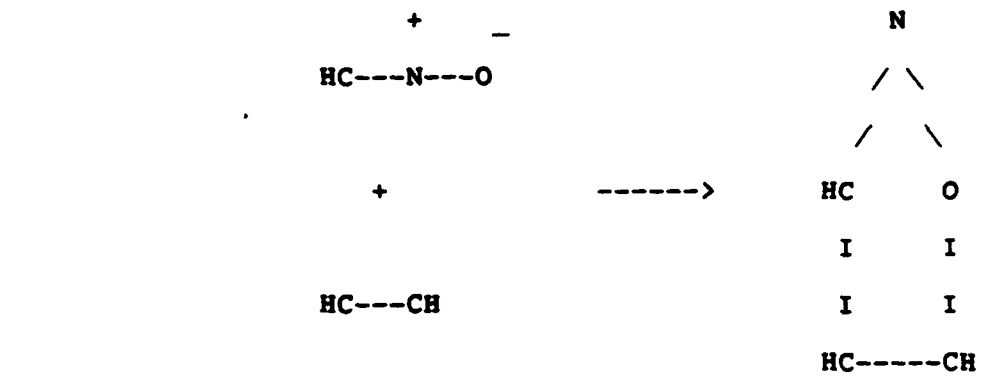
Schleyer, Pople et al. JACS 98 pg 5419 (1976)

Problem 7

Consider the following organic reactions:

i) [2+2] cycloaddition reaction between two ethylene molecules to give cyclobutane [1].

ii) 1,3 dipolar cycloaddition reaction of fulminic acid with acetylene [2]:



iii) [4+2] cycloaddition reaction between 1,3-butadiene and ethylene (Diels-Alder reaction) [3].

For each of these reactions consider some of the various approaches reported in refs. 1-3 (supra-supra and trans approaches for i,concerted approach for ii and supra-supra concerted approach for iii) and choose appropriate valence orbital spaces.

Subsequently perform CI (or MCSCF) computations [4] on reactant molecules at infinite separation using for the two fragments standard geometries or the optimum geometries of refs 1-3.

Transform the canonical valence molecular orbitals (CMO's) of the previous computations to localized orbitals (LMO's) using Boys'method [5] and performe an additional CI computation in the new representation. Compare and interpret the results obtained in the canonical and localized representation.

******

HINT: Let us take a simple example: two ethylene molecules in a supra-supra approach as shown in the scheme.

```
b      c
I      I
I      I              a,b ==> Ethyl. 1
a------d ----> z      d,c ==> Ethyl. 2
```

Using the Gaussian-82 series of programs [6] we perform simple MO computations (Extended Huckel, semiempirical or RHF computations) on the two fragments at infinite separation and in the chosen geometry.

These computations provide a set of molecular orbitals which can be used to perform the subsequent CI

computation (otherwise they can be used as starting orbitals for an MCSCF computation). Between these orbitals it is possible to choose an appropriate valence orbital sub-space which, for the above example, is given by the bonding and anti-bonding orbitals of pi symmetry of the two ethylene molecules.

The valence space orbitals are canonical molecular orbitals (CMO's): thus they are completely delocalized on each fragment. These orbitals can be easily transformed to a new set of orbitals,keeping the Total Energy of the system unchanged, if we use an appropriate unitary transformation. In particular, using the transformation suggested by Boys, we can obtain a set of localized orbitals (2pz atomic orbitals on each Carbon atom in the above example) which can be used for the final CI computation.

Important note: The CI (MCSCF) code runs as part (indipendent link with appropriate options) of Gaussian 82. An option allows the user to choose between a CI or an MCSCF computation. Another option can activate the Boys' localization procedure.

Furthermore, if the first computation is an MCSCF computation, the final CMO's must be saved for the subsequent job (Boys' localization and CI).

******

REFERENCES:

1. Bernardi,F.; Bottoni,A.; Robb,A.M.; Schlegel,H.B.; Tonachini,G. J.Am.Chem.Soc. 1985, 107, 2260.

2. Bernardi,F.; Bottoni,A.; McDouall,J.J.W.; Robb,M.A.; Shlegel,H.B. Faraday Symp.Chem.Soc. 1984, 19, 137

3. (a) Bernardi,F.; Bottoni,A.; Robb,M.A.; Field,M.J.; Hillier,I.H.;(b) Guest,M.F. J.Chem.Soc.Chem.Commun. 1985, 1052. (b) Bernardi,F.; Bottoni,A.; Venturini,A.; Robb,M.A.; Field,M.J.; Hillier,I.H. Guest,M.F. J.Am.Chem.Soc. in press.

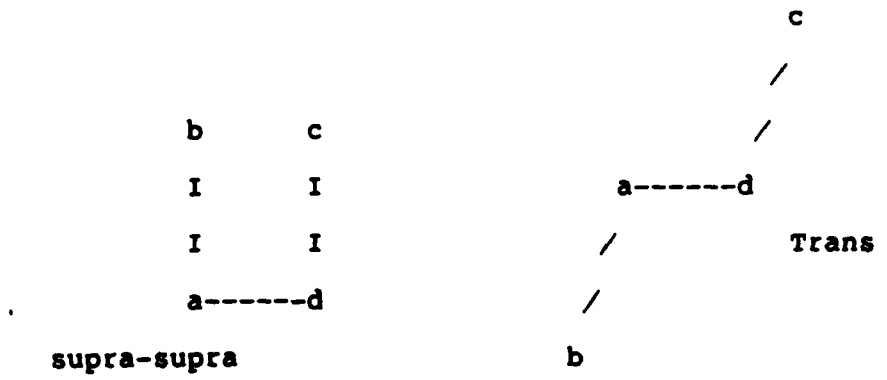
4. Hegarty,D; Robb,M.A. Mol.Phys. 1979,38,1795.

5. Boys,S.F. Rew.Mod.Phys. 1960,32,296.

6. Gaussian 82: Carnegie Mellon University, Binkley,J.S.; Whiteside,R.A.; Krishnan,R.;Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

Problem 8

For the cycloaddition reaction between two ethylene molecules [1] consider the two critical points located on the reaction surface for the supra-supra and the trans approaches shown in the scheme:



The first critical point corresponds to a second order saddle point (SOSP) and the second one to a transition state (TS): the corresponding geometries are reported in ref 1.

For these two structures, using the canonical fragment MO's at infinite separation of problem 1, performe a CI computation.

In a subsequent step, using the canonical fragment MO's of Problem 1 as starting orbitals, perform an MCSCF [2] computation on the two structures. Transform the final MO's (canonical MO's) to localized MO's (Boys' method [3]) and perform a CI computation.

Compare the various results.

******

HINT: The approach to follow for solving this problem is very similar to that suggested for Problem 1.

In particular we must run three different Gaussian 82 [4] jobs for both structures:

Job N.1: A simple CI using the fragment CMO's of Problem 1.

Job N.2: An MCSCF computation using as starting orbitals the previous fragment CMO's. It is important to remember to save the final optimum MCSCF orbitals for the subsequent run.

Job N.3: A CI computation after having localized the CMO's obtained in JOB N.2.

******

REFERENCES:

1. Bernardi,F.; Bottoni,A.; Robb,A.M.; Schlegel,H.B.; Tonachini,G. J.Am.Chem.Soc. 1985, 107, 2260.

2. Hegarty,D; Robb,M.A. Mol.Phys. 1979,38,1795.

3. Boys,S.F. Rew.Mod.Phys. 1960,32,296.

4. Gaussian 82: Carnegie Mellon University, Binkley,J.S.; Whiteside,R.A.; Krishnan,R.; Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

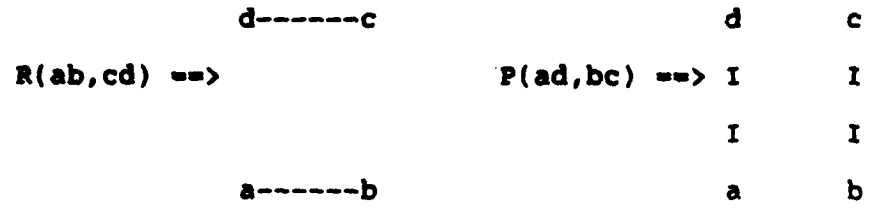
Problem 9

For the [2+2] cycloaddition reaction between two ethylene molecules [1] consider the transition structure corresponding to a trans approach between the reactants.

Using VB theory [2,3]] and Rumer diagrams [2,3,4] for describing the reactant and product bonding situations together with the results of an MCSCF computation in a localized basis, set up an appropriate diabatic decomposition scheme for this critical point.

******

HINT: This reaction, if we focus our attention only on the valence orbital space, can be treated in valence bond (VB) theory as a four electron problem. If we consider only covalent structures,the reactant and product bonding situations between the two molecules can be associated with the two following Rumer diagrams:



REACTANTS PRODUCTS

where a,b and c,d denote the atomic orbitals of 'pi' symmetry on the Carbon atoms of the first and second ethylene molecule respectively.

The two diabatic functions R(ab,cd) and P(ad,bc) (which are non orthogonal eigen-functions of the spin operator S2 with eigenvalue S(S+1) = 1) can be computed as linear combination of the six determinants characterized by an eigenvalue of the Sz operator equal to 0:

(a^bcd^) (a^b^cd) (a^bc^d)

(ab^cd^) (abc^d^) (ab^c^d)

where a represents the atomic orbital a associated with an alpha spin function and a^ is the same atomic orbital associated with a beta spin function.

This simple VB representation can be easily extracted from the results of an MCSCF computation on the optimum geometry of the trans TS, as follows:

i) Perform a full MCSCF computation on the TS structure and save the final MO's (Problem 2).

ii) Transform the canonical MO's (CMO's) obtained in the previous step to a set of localized MO's (LMO's) using Boys' method; perform a CI computation in the LMO basis using, for the CI expansion, a basis of Slater

determinants.

iii) using the CI results in the localized representation of the previous step, evaluate an effective Hamiltonian matrix in the basis of the above six determinants. To this purpose use Van Vleck method [5] to transform the Hamiltonian matrix (the CI matrix of ii) to a blocked matrix where the reference space corresponds to the six determinants necessary for describing covalent structures.

Note: An appropriate option in the MCSCF link can be used to activate Van Vleck method.

******

REFERENCES:

1. Bernardi,F.; Bottoni,A.; Robb,A.M.; Schlegel,H.B.; Tonachini,G. J.Am.Chem.Soc. 1985, 107, 2260.

2. Eyring,H; Walter,J; Kimball,G.E. "Quantum Chemistry" John Wiley & Sons Inc., New York.

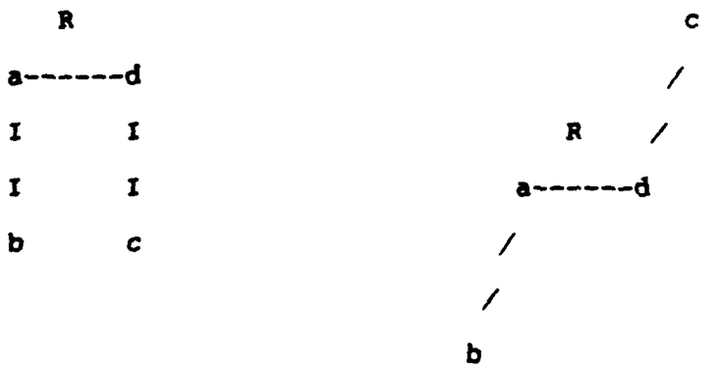
3. McWeeny,R; Sutcliffe,B.T. " Methods of Molecular Quantum Mechanics" Academic Press Inc., London, 1969.

4. Pauncz,R "Spin Eigenfunctions - Construction and use" Plenum Press, London, 1979.

5. Shavitt,I; Redmon,L.T. J.Chem.Phys. 1980,73,5711.

Problem 10

Consider the supra-supra and trans approaches for the [2+2] cycloaddition reaction between two ethylene molecules [1] as shown in the Scheme (a,b and c,d represent the two Carbon atom pairs of the two approaching molecules respectively).



supra-supra trans

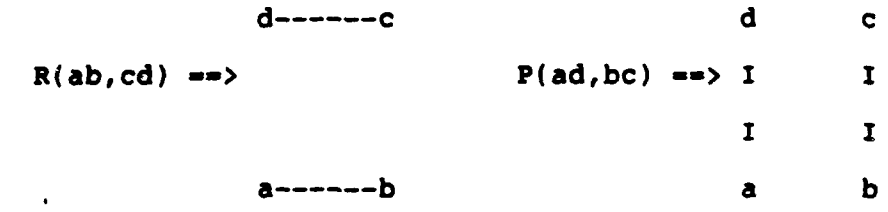
Scheme

Using Rumer covalent structures to represent the reactant and product bonding situation between the two molecules and the various Hamiltonian matrices reported in the following sections, calculate the energies of the reactant and product diabatic curves and the energies of the resulting adiabatic curves for various values of the approaching distance R (assumed here as reaction coordinate).

Show the behaviour of these curves in a diagram of the Energy versus R.

****

HINT: Following the line of Problem 3 write the two wave functions R and P which correspond to the two Rumer diagrams [2,3,4]:



in terms of the six determinants characterized by an eigenvalue of the Sz operator equal to 0 (Note that, in the two above Rumer diagrams, the symbols a,b,c,d denote either the four Carbon atoms or the corresponding 2p atomic orbitals involved in the bond changes). These six determinants, which form the representation for the Hamiltonian matrices, are ordered as follows:

1/// --> (a^bcd^) 2/// --> (a^b^cd) 3/// --> (a^bc^d)

4/// --> (ab^cd^) 5/// --> (abc^d^) 6/// --> (ab^c^d)

where a represents the atomic orbital a associated with an alpha spin function and a^ is the same atomic

orbital associated with a beta spin function.

To obtain the diabatic energies we must take the matrix products:

$$E(R) = H(R,R) = \langle R,H,R \rangle \qquad E(P) = H(P,P) = \langle P,H,P \rangle$$

where H corresponds to the Hamiltonian operator.

To obtain the energies of the resulting adiabatic curves E0 (ground state) and E1 (corresponding excited state) we must compute the non-diagonal matrix element between R and P:

$$H(R,P) = \langle R,H,P \rangle$$

and solve the corresponding 2X2 secular problem:

$$\begin{vmatrix} H(R,R) - E & H(R,P) - S(R,P)*E \\ H(R,P) - S(R,P)*E & H(P,P) - E \end{vmatrix} = 0$$

where S(R,P) represents the overlap between R and P

A simple Fortran program can be easily written for evaluating H(R,R), H(P,P), E0 and E1

******

The hamiltonian matrices for this problem will be found in a ready-to-use file.

REFERENCES:

1. Bernardi,F.; Bottoni,A.; Robb,A.M.; Schlegel,H.B.; Tonachini,G. J.Am.Chem.Soc. 1985, 107, 2260.

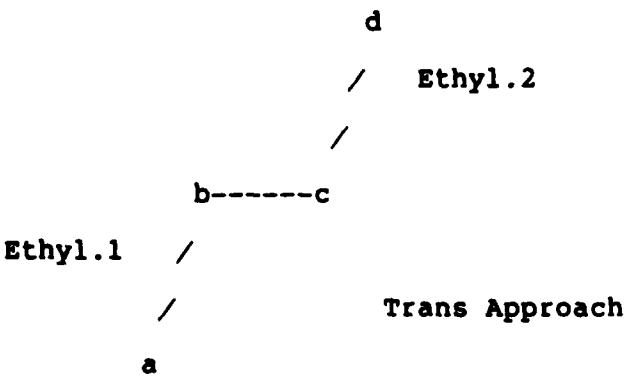
2. Eyring,H; Walter,J; Kimball,G.E. "Quantum Chemistry" John Wiley & Sons Inc., New York.

3. McWeeny,R; Sutcliffe,B.T. " Methods of Molecular Quantum Mechanics" Academic Press Inc., London, 1969.

4. Pauncz,R "Spin Eigenfunctions - Construction and use" Plenum Press, London, 1979.

Problem 11

Consider the [2+2] cycloaddition reaction between two ethylenes. For this reaction, using MCSCF [1] gradient [2] method and with a minimal STO-3G basis set [3], compute the optimum geometry of the fragmentation transition state corresponding to a trans approach between the two molecules [4]:



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HINT: MCSCF code and associated gradient codes can be used as part (indipendent links) of the gaussian-82 series of programs [5].

The geometry optimization for the above critical point can be performed in the three following steps:
i) Perform a single MCSCF computation on the two molecules at infinite distance using Extended Huckel MOs as starting MOs for the MCSCF process: save the final

MCSCF molecular orbitals (see Problem 1).

ii) Using the MOs obtained in the previous step perform a single MCSCF computation at bond distance. In this case, where we are looking for a transition state, the bond distance (a---d in the previous scheme) will be longer than a normal C-C bond distance. A good starting geometry can be obtained from ref.4. Save the final MCSCF MOs (see Problem 2).

iii) Using the MOs obtained in step ii) start the geometry optimization run. Use a reasonable starting value for the diagonal element of the Hessian matrix corresponding to the reaction coordinate (a---d).

******

REFERENCES:

1. Hegarty,D; Robb,M.A. Mol.Phys. 1979,38,1795.

2. Schlegel,H.B.; Robb,M.A. Chem. Phys. Lett. 1982, 93, 43.

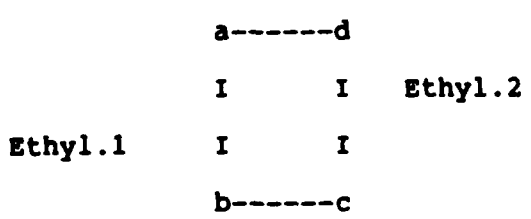
3. Hehre,W.J.; Stewart,R.F. Pople,J.A. J.Chem.Phys. 1969,51,2657.

4. Bernardi,F; Robb,M.A.; Schlegel, H.B. Tonachini,G. J.Am.Chem.Soc. 1984,106,1198

5. Gaussian 82: Carnegie Mellon University, Binkley,J.S.; Whiteside,R.A.;Krishnan,R.; Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

Problem 12

Consider the [2+2] cycloaddition reaction between two ethylenes. For this reaction, using MCSCF [1] gradient [2] method and with a minimal STO-3G basis set [3], compute the optimum geometry for the critical point corresponding to a supra-supra approach between the two molecules [4]:



supra-supra Approach

Characterize the nature of this critical point by a numerical computation of the corresponding Hessian matrix.

******

HINT: MCSCF code and associated gradient codes can be used as part (indipendent links) of the gaussian-82 series of programs [5].

The geometry optimization for the above critical point can be performed in the three following steps:

i) Perform a single MCSCF computation on the two molecules at infinite distance using Extended Huckel MOs as starting MOs for the MCSCF process; save the final MCSCF molecular orbitals (see Problem 1).

ii) Using the MOs obtained in the previous step perform a single MCSCF computation at bond distance. A good starting geometry can be obtained from ref.4. Save the final MCSCF MOs (see Problem 2).

iii) Using the MOs obtained in step ii) start the geometry optimization run. Use a reasonable starting value for the diagonal element of the Hessian matrix corresponding to the reaction coordinate.

iv) Compute the Hessian matrix for the final geometry by the method of finite differences (star-only method).

******

REFERENCES:

1. Hegarty,D; Robb,M.A. Mol.Phys. 1979,38,1795.

2. Schlegel,H.B.; Robb,M.A. Chem. Phys. Lett. 1982, 93, 43.

3. Hehre,W.J.; Stewart,R.F. Pople,J.A. J.Chem.Phys. 1969,51,2657.

4. Bernardi,F; Robb,M.A.; Schlegel, H.B. Tonachini,G. J.Am.Chem.Soc. 1984,106,1198

5. Gaussian 82: Carnegie Mellon University,

Binkley,J.S.; Whiteside,R.A.;Krishnan,R.; Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

Problem 13

The electric reaction field may induce important electronic and nuclear relaxation effects. Amides are especially well suited to study this effect, because ionic structures (in a Valence Bond language) will have a meaningful weight, which will be largely modified upon introduction of a reaction field. This translates into an important electronic and relaxation effect.

The purpose of this problem is to study this effect in the formamide molecule, HCONH2.

Suggested Plan of Attack

1) Optimize the geometry of the formamide molecule by means of the MNDO semiempirical method. From the charge distribution, discuss the ressonant structures that intervene in the wavefunction.

2) By using the spherical cavity model for the solvent, study the electronic relaxation owing to the reaction field, when no reoptimization is performed. Discuss the new charge distribution. The experimental volume of formamide is 65.990 A**3.

3) With the spherical cavity model, reoptimize the geometry of the formamide molecule, so the nuclear relaxation owing to solvent effect may be studied. Discuss again the charge distribution obtained.

REFERENCES

1) J. Bertran, A. Oliva, D. Rinaldi, J.L.Rivail, Nouv. J. Chimie, 4, 209 (1980)

2) D. Rinaldi, Computers and Chemistry, 1, 108(1976)

3) Program GEOMO, QCPE No. 290.

4) E. Sanchez Marcos, J. Maraver, M. F. Ruiz-Lopez and J. Bertran, Can. J. Chem., 2353, 64(1986)

Problem 14

The site of attack of benzene derivatives by nucleophiles or electrophiles has been interpreted through two static indexes: the charge index if the reaction is charge-controlled, and the frontier orbitals if the reaction if orbital-controlled. Most experimental data refer to studies in solution, sp charges and frontier orbitals may be dramatically altered by the presence of the solvent. Moreover, given the different charge distribution of the orto, meta and para adducts, the solvation energy in each of them can be also very different.

The goal of this problem is to study which factors determine the relative reactivity order when the reaction is carried out in solution. The benzonitryle molecule is taken as an example of benzene derivative. The semiempirical MNDO method will be used thoroughout.

Suggested Plan of Attack

---1---

a) Optimize the benzonitryle geometry and analyze the obtained static indexes.

b) Study in gas-phase: Entry of H+ and H- at the orto, meta, and para positions (minimization of intermediates only). Analyze the relative reactivity order, and discuss versus charge indexes and frontier orbitals of benzonitryle.

a) With the ellipsoidal cavity to model the solvent, and using the experimental volume of 169.528 A**3, carry out new energy calculations on optimized gas-phase neutral geometries. Use water as solvent (dielectric constant 78). Analyze new dipole moments, charge distribution and frontier orbitals.

b) Also by means of the ellipsoidal cavity model for the solvent, study the intermediates optimized in the gas phase with H+ or H- under solvent effect. Analyze the relative order of energies between the three isomers. Compare with gas-phase results, and discuss the influence of the solvation energy.

REFERENCES

1) J. Bertran, A. Oliva, D. Rinaldi, J.L.Rivail, Nouv. J. Chimie, 4, 209 (1980)

2) D. Rinaldi, Computers and Chemistry, 1, 108(1976)

3) Program GEOMO, QCPE No. 290.

4) E. Sanchez Marcos, J. Maraver, M. F. Ruiz-Lopez and J. Bertran, Can. J. Chem., 2353, 64(1986)

Problem 15

Influence of solvent on the Walden inversion reaction.

In this psoblem the solvent effect on the Walden Inversion Reaction on the (FCH3F)- system will be studied. The semiempirical AM1 method will be used for that purpose. Experimentally the inversion barrier in solution is about 25 kcal/mol. When theoretical calculations are carried out on the gas-phase reaction, a double-well profile appears. The purpose of this study is to determine the reaction profile in solution. Two ways to represent the solvent will be used: a discrete one, where each fluorine atom is attached to one water molecule, and a continuum one, where the (FCH3F)- system is placed into a cavity opened in the solute.

Suggested plan of attack:

Gas-phase:

1) Optimize at the AM1 level the gas-phase reactants.

2) Locate a possible intermediate for the F(-)...CH3F complex.

3) Locate the transition state of the reaction. This can be accomplished in two ways: a) by means of the AMPAC program, the SIGMA keyword (minimization of the gradient norm) can be used. b) The GEOMO program can be used, where the two F-C distances can be made the same by symmetry, and the hydrogens may be forced to be perpendicular to the F-C-F axis.

4) Get the force constants and vibrational modes for all species.

Discrete representation for the solvent:

5-8) Repeat steps 1-4 but with one water molecule attached to each fluorine. The O-H-F angle must always be forced to be linear or quasi-linear.

Continuum representation for the solvent:

The GEOMO program will be used necessarily in this step. The volumes (in angstrom**3) of the spherical cavities for each species are: F-, 33.593; CH3F, 108.366; INT, 131.699, and TS 158.117. The volumes for reactants have been obtained from experimental data. For the intermediate and the transition state, they have been obtained though extrpolation from the Claussius-Mossoti relation between polarizabilities and volume.

9) Compute the solvation energy for each species with solvent dielectric constant 78 (i.e., for water). Construct new energy profile.

REFERENCES

1) J. Bertran, A. Oliva, D. Rinaldi, J.L.Rivail, Nouv. J. Chimie, 4, 209 (1980)

2) D. Rinaldi, Computers and Chemistry, 1, 108(1976)

3) Program GEOMO, QCPE No. 290.

Problem 16

Application of variational transition state theory to

$OH + H2 \longrightarrow H2O + H$ with harmonic approximation.

Conventional Transition State Theory (TST) may be interpreted as a calculation of the free energy of activation under the assumption that a configuration space dividing surface, located at the highest-potential-energy point (Saddle point) on the minimum-potential-energy path (MEP), provides a perfect bottleneck to reaction, i.e., that recrossing effects are negligible for such a dividing surface. Because recrossing usually occurs, TST rate constant will overestimate the exact classical result. To improve TST, in Canonical Variational Transition State Theory (CVT) location of the configuration-space dividing surface or Generalized Transition State (GTS), through which the equilibrium flux in the product direction is calculated, is optimized variationally as a function of the location s where it intersects the MEP, in order to obtain the minimum rate constant at a given Temperature. So, CVT locates Canonical Variational Transition State at the highest-free- energy-of-activation point on the MEP. A threshold-corrected version of CVT is called Improved Canonical Variational Theory (ICVT).

In this problem with the POLYRATE program, one will apply CVT and ICVT to the reaction $OH + H2 \longrightarrow H2O + H$, using the analytic potential energy surface obtained by Schatz and Elgersma by a fit to the ab initio calculations of Walch and Dunnning. Vibrational modes of the reactants, products and GTS are assumed to be harmonic.

Suggested plan of attack

1) Make a normal mode analysis of reactants, products and saddle point.

2) Construct the MEP and draw several geometries of the supermolecule along MEP.

3) Represent the classical potential energy (VMEP), the zero-point energy and the vibrationally adiabatic ground-state potential energy (VA) as functions of the distance (s) along the MEP from the saddle point. Locate the maximum value of VA.

4) Make a vibrational-mode correlation analysis along s : plot the frequencies versus s for the various nornal modes and identify the character of each mode as fuction of s.

5) Represent $\Delta G^{GT,O}$ (CVT) and $\Delta G^{GT,O}$ (ICVT) versus s at several Temperatures (T).

6) Find the Canonical Variational and the Improved Canonical Variational Transition States at different T.

7) Calculate the transmission coefficients by several ways, in order to model the quantal effects on reaction-coordinate motion at several T.

8) Calculate TST, CVT and ICVT forward and reverse rate constants at several T. Compare the obtained values with the experimental data:

T(K)	k(cm3 Molecule-1 seg-1)
298	6.08 + 0.37 E-15
400	3.7 + 1.1 E-14
600	2.9 + 0.9 E-13
1000	2.4 + 0.7 E-12

9) Calculate the Equilibrum Constants.

10) Make a factor ratio analysis of CVT and TST rate constants.

11) Make a global discussion of results.

Problem 17

Application of variational transition state theory to

$OH + H2 \longrightarrow H2O + H$ With inclusion of anharmonicity

In general, the vibrational degrees of freedom of the reactants, products and GTS are bound by an anharmonic potential which contains terms in normal coordinates of order higher than two. Substantial differences can be obtained between rate constants computed from harmonic and anharmonic vibrations. In this problem, one will study the reaction $OH + H2 \longrightarrow H2O + H$ with anharmonicity modeled by the Morse I- quadratic-quartic approximation.

Suggested plan of attack

Repeat the preceding problem including now the anharmonicity. Take into account that it is not necessary to calculate again each step because a lot of results are invariant upon introduction of anharmonicity. Compare the results obtained in both cases.

Problem 18

Application of the statistical-diabatic model for state-selected reaction rates to

$$OH\ (nOH) + H2\ (nHH) \longrightarrow H2O + H\ .$$

In this problem a vibrationally diabatic version of Variational Transition State Theory is employed to calculate the rate constants k(nOH ,nHH ,T) for the vibrational-state-selected reaction $OH\ (nOH) + H2\ (nHH) \longrightarrow H2O + H$, where the rotational and traslational degrees of freedom are at Temperature T . The experimental results have shown that excitation of the bond to be broken (H2) has a large effect on the rate constant and excitation of the spectator (O-H) bond has a small effect.

The Schatz-Elgersma analytic potential energy surface is used and the Morse I quadratic-quartic approximation for anharmonicity is adopted.

Suggested plan of attack

Repeat the steps 3,5,6,7,8,9,10 and 11 of the problem 16, for the three following cases:

A) nOH = 0 nHH = 0

B) nOH = 1 nHH = 0

C) nOH = 0 nHH = 1

Compare each case with the completely thermally averaged reaction rates.

List of references for Problems 16,17, and 18.

[1] D.G. Truhlar, A.D. Isaacson and B.C. Garrett, "Theory of Chemical Reaction Dynamics", Vol. IV, M. Baer, Ed., CRC Press, Boca Raton, FL, 1985.

[2] A.D. Isaacson, D.G. Truhlar, S.N. Rai, R. Steckler, G.C. Hancock, B.C. Garrett and M.J. Redmon, Comp. Phys. Comm, 47, 91 (1987).

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[5] S.P. Walch and T.H. Dunning, J. Chem. Phys., 72, 1303 (1980).

[6] A.D. Isaacson and D.G. Truhlar, J. Chem. Phys., 76, 1380 (1982).

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Suggested Computational Problems

NATO Advanced Study Institute

NEW THEORETICAL CONCEPTS FOR UNDERSTANDING ORGANIC REACTIONS

19th June - 2nd July 1988

Sant Feliu de Guíxols, Spain

Tutors

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Problem 2

Double rotors with 2 torsional angles: x1 and x2, associated with the systems of fully hydrogenated molecules of the type X-Z-Y will be subjected to conformational study. This study is analogous to those of PART I but the SCF energy grid points are expected to be evaluated within the school. Because of time limitations STO-3G basis set will be used in evaluating the SCF grid points and the molecular geometry will not necessarily be optimized. The least amount of problem expected when the central atom is carbon (Z=C) and X as well as Y may be C, N or O.

C-C-C	C-C-N	C-C-O
	N-C-N	N-C-O
		O-C-O

The simplest of these species is CH3-CH2-CH3 located at the upper left hand corner of the above hemi-matrix. The other two hemi-matrices with Z=N and Z=O have a similar set of fully hydrogenated compounds that may pose certain problems at the level of SCF convergence.

Problem 3

The generated and fitted potential energy surfaces will be subjected to topological analysis. First of all the first derivatives of equation (3) for surfaces and equation (4) for hypersurfaces will be evaluated and be set equal to zero in order to locate the whereabouts of the critical points. Subsequently, at the location of each of the critical points the second derivatives of E (from equations 3 and 4 for surfaces and hpersurfces respectively) will be evaluated in order to determine the order (L) of the critical points a surface may have. For a minimum L=0, and for a transition state L=1. The value of L=2 is a maximum for a surface and supersaddle point for a hypersurface. The maximum for a hypersurface has a characteristic L=3 value.

Conformational surfaces obey the following alternating sum rule for the number of critical points (NL), where L will run from o to n and n is the dimensionality of the problem. (For surfaces n=2 and hypersurfaces n=3)

$$\text{sum } [(-1)^{**}L]\ NL = 0 \qquad (5)$$

For an ideal surface

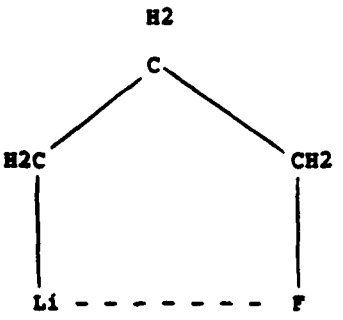
$$Nl = ml.m2.BL \qquad (6)$$

and for an ideal hypersurface

$$N1 = m1.m2.m3.BL \qquad (7)$$

where mi's represent the topological periodicity along each of the one dimensional location. BL is the Betti numbers which are the binomial coefficients (n over L) for conformational problems.

Certain chemical systems with too much repulsive or too much attractive interaction will not obey equations (6) or (7). Those who wish to explore such unique conformational situations might attempt to study the following molecule



with two torsional angles (x1 and x2) along the pair of C-C bonds. This disubstituted propane is expected to show a markedly different potential energy surface topology in comparison to that of unsubstituted propane.

Problem 4

HCN-HNC Rearrangement

The HCN -> HNC reaction has been used frequently to illustrate transition structure optimization methods. At the HF/STO-3G level, the reactant geometry is: R(CN)=1.153 A, R(CH)=1.070 A (linear); the product geometry is: R(CN)=1.170 A, R(NH)=1.011 A (linear). In this project with GAUSSIAN 86, you will use the linear synchronous transit(LST method to get near the transition state and gradient optimization methods to locate it exactly.

Suggested plan of attack:

(1) Starting from the reactants and products, use the linear synchronous transit method to locate the transition structure approximately.

(2) Calculate the gradient and frequency at the LST optimized structure. Is it a stationary point? Is it a saddle point?

(3) Optimize the transition structure using OPT=TS. Don't forget to have the program calculate a few critical force constants.

(4) Test the optimized transition state by calculating the frequencies.

References:

LST: Halgren and Lipcomb, CPL 49 pg 225 (1977)

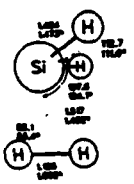
TS opt: Schlegel, Adv.Chem.Phys. 67 pg 249 (1987), J.Comp.Chem. 3 pg 214 (1982)

HCN ts: Ishida, Morokuma and Kormornicki: JCP 66 pg 2153 (1977)

Problem 5

SiH2 + H2 -> SiH4 Insertion Reaction

The ground state of SiH2 is a singlet with an sp2 lone pair. Like singlet carbene, SiH2 inserts readily into covalent bonds. The least motion pathway would proceed through a C2v symmetry transition state (sp2 lone pair pointing at the H2 sigma bond). However, this path is forbidden by orbital symmetry, and the reaction goes via a non-least motion pathway. The allowed transition state has Cs symmetry with the sp2 lone pair of SiH2 nearly parallel to H2.



The geometry of the reactants is R(SiH)=1.531 A, <HSiH=93.8 R(H2)=0.735 A; for the product R(SiH)=1.487 (all data at HF/3-21G). The transition state has a 50 percent elongation of the H2 bond. In this project, GAUSSIAN 86 will be used to determine the transition state at the HF/3-21G level.

Suggested plan of attack:

(1) Construct several different Z-matrix coordinate systems for the transition state. Choose the best coordinate system for the rest of the calculations.

(2) Calculate the energy and gradients at several points along an approximate reaction path to get a rough location of the transition state.

(3) Optimize the transition structure using gradients. Start with an analytically calculated Hessian (the CALCFC option).

(4) Test the transition state by calculating the vibrational frequencies. Sketch the transition vector and the transition structure.

(5) Draw an orbital interaction diagram for the transition state and discuss why the non-least motion pathway is allowed but the least motion pathway is forbidden.

References:

Fleming: Frontier Orbitals and Organic Chemical Reactions.

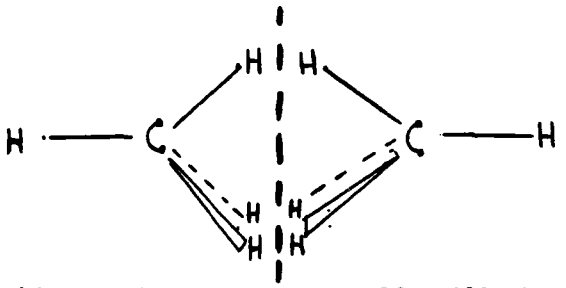
Colvin, Grev, Schaefer and Bicerano: CPL 99 pg 399 (1983)

Sosa and Schlegel: JACS 106 pg 5847 (1984)

Problem 6

Planar tetracoordinated carbon and the inversion of CH4

The possibility of planar tetracoordinated carbon has long fascinated theoretical and experimental chemists. The simplest hydrocarbon, CH4 (Td symmetry), can be distorted planar (D4h symmetry). Planar methane is a potential transition state for the inversion of configuration of tetrahedral methane to give its mirror image.



In this project, GAUSSIAN 86 will be used to explore the potential energy surface of methane at the HF/3-21G level. The aim of the exercise is to illustrate higher order saddle points and how to get to lower order saddle points, and eventually to the transition state (first order saddle point).

Suggested plan of attack.

(1) Optimize tetrahedral methane.

(2) Optimize planar methane (D4h) and calculate the frequencies. Is it a transition state (first order saddle point)?

(3) Displace the structure along any one of the normal modes with an imaginary frequency (except for the mode that leads to the Td minimum).

(4) Optimize the distorted structure and calculate the frequencies. If it is not a first order saddle point, go back to (3).

(5) Make a sketch of the methane potential energy surface indicating the energetics and connectivity of the minima and the various first and higher order saddle points.

References.

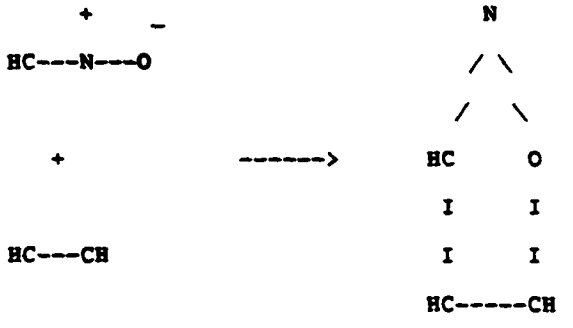
Schleyer, Pople et al. JACS 98 pg 5419 (1976)

Problem 7

Consider the following organic reactions:

i) [2+2] cycloaddition reaction between two ethylene molecules to give cyclobutane [1].

ii) 1,3 dipolar cycloaddition reaction of fulminic acid with acetylene [2]:



iii) [4+2] cycloaddition reaction between 1,3-butadiene and ethylene (Diels-Alder reaction) [3].

For each of these reactions consider some of the various approaches reported in refs. 1-3 (supra-supra and trans approaches for i,concerted approach for ii and supra-supra concerted approach for iii) and choose appropriate valence orbital spaces.

Subsequently perform CI (or MCSCF) computations [4] on reactant molecules at infinite separation using for the two fragments standard geometries or the optimum geometries of refs 1-3.

Transform the canonical valence molecular orbitals (CMO's) of the previous computations to localized orbitals (LMO's) using Boys'method [5] and performe an additional CI computation in the new representation. Compare and interpret the results obtained in the canonical and localized representation.

******

HINT: Let us take a simple example: two ethylene molecules in a supra-supra approach as shown in the scheme.

```
b      c
I      I
I      I            a,b ==> Ethyl. 1
a-------d ----> z   d,c ==> Ethyl. 2
```

Using the Gaussian-82 series of programs [6] we perform simple MO computations (Extended Huckel, semiempirical or RHF computations) on the two fragments at infinite separation and in the chosen geometry.

These computations provide a set of molecular orbitals which can be used to perform the subsequent CI

computation (otherwise they can be used as starting orbitals for an MCSCF computation). Between these orbitals it is possible to choose an appropriate valence orbital sub-space which, for the above example, is given by the bonding and anti-bonding orbitals of pi symmetry of the two ethylene molecules.

The valence space orbitals are canonical molecular orbitals (CMO's): thus they are completely delocalized on each fragment. These orbitals can be easily transformed to a new set of orbitals,keeping the Total Energy of the system unchanged, if we use an appropriate unitary transformation. In particular, using the transformation suggested by Boys, we can obtain a set of localized orbitals (2pz atomic orbitals on each Carbon atom in the above example) which can be used for the final CI computation.

Important note: The CI (MCSCF) code runs as part (indipendent link with appropriate options) of Gaussian 82. An option allows the user to choose between a CI or an MCSCF computation. Another option can activate the Boys' localization procedure.

Furthermore, if the first computation is an MCSCF computation, the final CMO's must be saved for the subsequent job (Boys' localization and CI).

******

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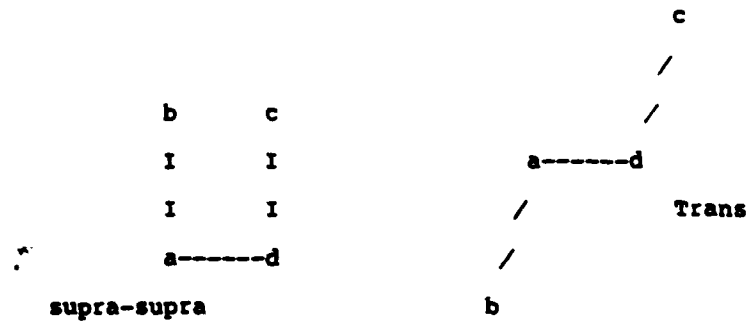
Problem 8

For the cycloaddition reaction between two ethylene molecules [1] consider the two critical points located on the reaction surface for the supra-supra and the trans approaches shown in the scheme:



The first critical point corresponds to a second order saddle point (SOSP) and the second one to a transition state (TS): the corresponding geometries are reported in ref 1.

For these two structures, using the canonical fragment MO's at infinite separation of problem 1, performe a CI computation.

In a subsequent step, using the canonical fragment MO's of Problem 1 as starting orbitals, perform an MCSCF [2] computation on the two structures. Transform the final MO's (canonical MO's) to localized MO's (Boys' method [3]) and perform a CI computation.

Compare the various results.

******

HINT: The approach to follow for solving this problem is very similar to that suggested for Problem 1.

In particular we must run three different Gaussian 82 [4] jobs for both structures:

Job N.1: A simple CI using the fragment CMO's of Problem 1.

Job N.2: An MCSCF computation using as starting orbitals the previous fragment CMO's. It is important to remember to save the final optimum MCSCF orbitals for the subsequent run.

Job N.3: A CI computation after having localized the CMO's obtained in JOB N.2.

******

REFERENCES:

1. Bernardi,F.; Bottoni,A.; Robb,A.M.; Schlegel,H.B.; Tonachini,G. J.Am.Chem.Soc. 1985, 107, 2260.

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3. Boys,S.F. Rew.Mod.Phys. 1960,32,296.

4. Gaussian 82: Carnegie Mellon University, Binkley,J.S.; Whiteside,R.A.; Krishnan,R.; Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

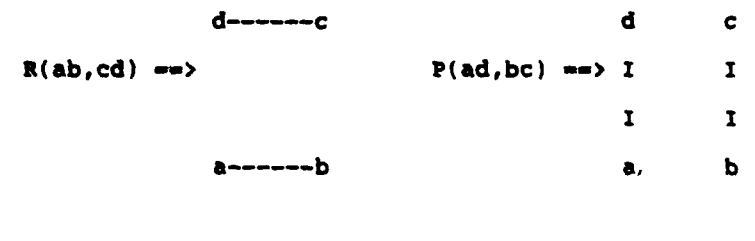
Problem 9

For the [2+2] cycloaddition reaction between two ethylene molecules [1] consider the transition structure corresponding to a trans approach between the reactants.

Using VB theory [2,3]] and Rumer diagrams [2,3,4] for describing the reactant and product bonding situations together with the results of an MCSCF computation in a localized basis, set up an appropriate diabatic decomposition scheme for this critical point.

******

HINT: This reaction, if we focus our attention only on the valence orbital space, can be treated in valence bond (VB) theory as a four electron problem. If we consider only covalent structures,the reactant and product bonding situations between the two molecules can be associated with the two following Rumer diagrams:



REACTANTS PRODUCTS

where a,b and c,d denote the atomic orbitals of 'pi' symmetry on the Carbon atoms of the first and second ethylene molecule respectively.

The two diabatic functions R(ab,cd) and P(ad,bc) (which are non orthogonal eigen-functions of the spin operator S2 with eigenvalue S(S+1) = 1) can be computed as linear combination of the six determinants characterized by an eigenvalue of the Sz operator equal to 0:

(a^bcd^) (a^b^cd) (a^bc^d)

(ab^cd^) (abc^d^) (ab^c^d)

where a represents the atomic orbital a associated with an alpha spin function and a^ is the same atomic orbital associated with a beta spin function.

This simple VB representation can be easily extracted from the results of an MCSCF computation on the optimum geometry of the trans TS, as follows:

i) Perform a full MCSCF computation on the TS structure and save the final MO's (Problem 2).

ii) Transform the canonical MO's (CMO's), obtained in the previous step to a set of localized MO's (LMO's) using Boys' method; perform a CI computation in the LMO basis using, for the CI expansion, a basis of Slater

determinants.

iii) using the CI results in the localized representation of the previous step, evaluate an effective Hamiltonian matrix in the basis of the above six determinants. To this purpose use Van Vleck method [5] to transform the Hamiltonian matrix (the CI matrix of ii) to a blocked matrix where the reference space corresponds to the six determinants necessary for describing covalent structures.

Note: An appropriate option in the MCSCF link can be used to activate Van Vleck method.

******

REFERENCES:

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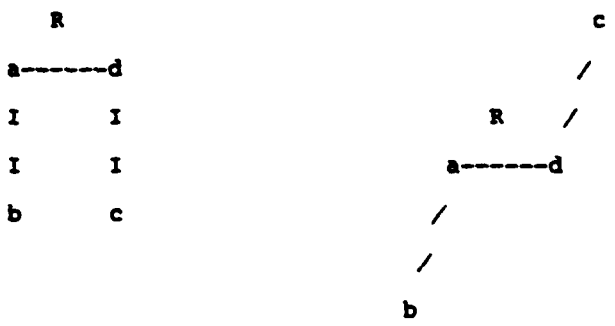
5. Shavitt,I; Redmon,L.T. J.Chem.Phys. 1980,73,5711.

Problem 10

Consider the supra-supra and trans approaches for the [2+2] cycloaddition reaction between two ethylene molecules [1] as shown in the Scheme (a,b and c,d represent the two Carbon atom pairs of the two approaching molecules respectively).



supra-supra trans

Scheme

Using Rumer covalent structures to represent the reactant and product bonding situation between the two molecules and the various Hamiltonian matrices reported in the following sections, calculate the energies of the reactant and product diabatic curves and the energies of the resulting adiabatic curves for various values of the approaching distance R (assumed here as reaction coordinate).

Show the behaviour of these curves in a diagram of the Energy versus R.

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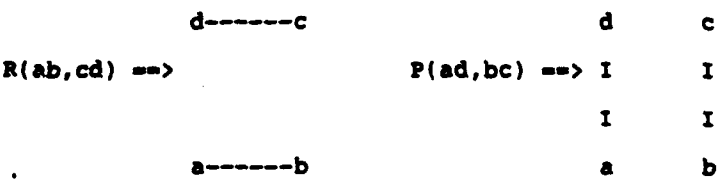
HINT: Following the line of Problem 3 write the two wave functions R and P which correspond to the two Rumer diagrams [2,3,4]:



in terms of the six determinants characterized by an eigenvalue of the Sz operator equal to 0 (Note that, in the two above Rumer diagrams, the symbols a,b,c,d denote either the four Carbon atoms or the corresponding 2p atomic orbitals involved in the bond changes). These six determinants, which form the representation for the Hamiltonian matrices, are ordered as follows:

1/// --> (a^bcd^) 2/// --> (a^b^cd) 3/// --> (a^bc^d)

4/// --> (ab^cd^) 5/// --> (abc^d^) 6/// --> (ab^c^d)

where a represents the atomic orbital a associated with an alpha spin function and a^ is the same atomic

orbital associated with a beta spin function.

To obtain the diabatic energies we must take the matrix products:

$$E(R) = H(R,R) = \langle R,H,R \rangle \qquad E(P) = H(P,P) = \langle P,H,P \rangle$$

where H corresponds to the Hamiltonian operator.

To obtain the energies of the resulting adiabatic curves E0 (ground state) and E1 (corresponding excited state) we must compute the non-diagonal matrix element between R and P:

$$H(R,P) = \langle R,H,P \rangle$$

and solve the corresponding 2X2 secular problem:

$$\begin{vmatrix} H(R,R) - E & H(R,P) - S(R,P)*E \\ H(R,P) - S(R,P)*E & H(P,P) - E \end{vmatrix} = 0$$

where S(R,P) represents the overlap between R and P

A simple Fortran program can be easily written for evaluating H(R,R), H(P,P), E0 and E1

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The hamiltonian matrices for this problem will be found in a ready-to-use file.

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1. Bernardi,F.; Bottoni,A.; Robb,A.M.; Schlegel,H.B.; Tonachini,G. J.Am.Chem.Soc. 1985, 107, 2260.

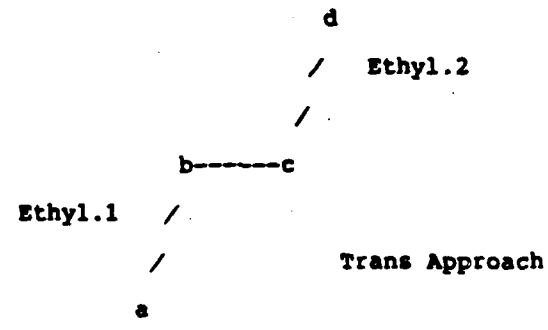
2. Eyring,H; Walter,J; Kimball,G.E. "Quantum Chemistry" John Wiley & Sons Inc., New York.

3. McWeeny,R; Sutcliffe,B.T. " Methods of Molecular Quantum Mechanics" Academic Press Inc., London, 1969.

4. Pauncz,R "Spin Eigenfunctions - Construction and use" Plenum Press, London, 1979.

Problem 11

Consider the [2+2] cycloaddition reaction between two ethylenes. For this reaction, using MCSCF [1] gradient [2] method and with a minimal STO-3G basis set [3], compute the optimum geometry of the fragmentation transition state corresponding to a trans approach between the two molecules [4]:



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HINT: MCSCF code and associated gradient codes can be used as part (indipendent links) of the gaussian-82 series of programs [5].

The geometry optimization for the above critical point can be performed in the three following steps:
i) Perform a single MCSCF computation on the two molecules at infinite distance using Extended Huckel MOs as starting MOs for the MCSCF process: save the final

MCSCF molecular orbitals (see Problem 1).

ii) Using the MOs obtained in the previous step perform a single MCSCF computation at bond distance. In this case, where we are looking for a transition state, the bond distance (a---d in the previous scheme) will be longer than a normal C-C bond distance. A good starting geometry can be obtained from ref.4. Save the final MCSCF MOs (see Problem 2).

iii) Using the MOs obtained in step ii) start the geometry optimization run. Use a reasonable starting value for the diagonal element of the Hessian matrix corresponding to the reaction coordinate (a---d).

******

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1. Hegarty,D; Robb,M.A. Mol.Phys. 1979,38,1795.

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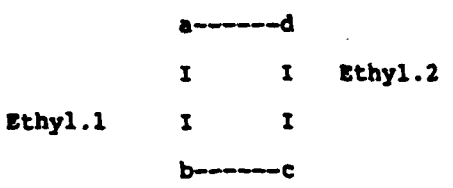
3. Hehre,W.J.; Stewart,R.F. Pople,J.A. J.Chem.Phys. 1969,51,2657.

4. Bernardi,F; Robb,M.A.; Schlegel, H.B. Tonachini,G. J.Am.Chem.Soc. 1984,106,1198

5. Gaussian 82: Carnegie Mellon University, Binkley,J.S.; Whiteside,R.A.;Krishnan,R.; Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

Problem 12

Consider the [2+2] cycloaddition reaction between two ethylenes. For this reaction, using MCSCF [1] gradient [2] method and with a minimal STO-3G basis set [3], compute the optimum geometry for the critical point corresponding to a supra-supra approach between the two molecules [4]:



supra-supra Approach

Characterize the nature of this critical point by a numerical computation of the corresponding Hessian matrix.

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HINT: MCSCF code and associated gradient codes can be used as part (indipendent links) of the gaussian-82 series of programs [5].

The geometry optimization for the above critical point can be performed in the three following steps:

i) Perform a single MCSCF computation on the two molecules at infinite distance using Extended Huckel MOs as starting MOs for the MCSCF process; save the final MCSCF molecular orbitals (see Problem 1).

ii) Using the MOs obtained in the previous step perform a single MCSCF computation at bond distance. A good starting geometry can be obtained from ref.4. Save the final MCSCF MOs (see Problem 2).

iii) Using the MOs obtained in step ii) start the geometry optimization run. Use a reasonable starting value for the diagonal element of the Hessian matrix corresponding to the reaction coordinate.

iv) Compute the Hessian matrix for the final geometry by the method of finite differences (star-only method).

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REFERENCES:

1. Hegarty,D; Robb,M.A. Mol.Phys. 1979,38,1795.

2. Schlegel,H.B.; Robb,M.A. Chem. Phys. Lett. 1982, 93, 43.

3. Hehre,W.J.; Stewart,R.F. Pople,J.A. J.Chem.Phys. 1969,51,2657.

4. Bernardi,F; Robb,M.A.; Schlegel, H.B. Tonachini,G. J.Am.Chem.Soc. 1984,106,1198

5. Gaussian 82: Carnegie Mellon University,

Binkley,J.S.; Whiteside,R.A.;Krishnan,R.; Seeger,R.; De Frees,D.J.; Schlegel,H.B.; Topiol,S.; Kahn,L.R.; Pople,J.A.

Problem 13

The electric reaction field may induce important electronic and nuclear relaxation effects. Amides are especially well suited to study this effect, because ionic structures (in a Valence Bond language) will have a meaningful weight, which will be largely modified upon introduction of a reaction field. This translates into an important electronic and relaxation effect.

The purpose of this problem is to study this effect in the formamide molecule, HCONH2.

Suggested Plan of Attack

1) Optimize the geometry of the formamide molecule by means of the MNDO semiempirical method. From the charge distribution, discuss the ressonant structures that intervene in the wavefunction.

2) By using the spherical cavity model for the solvent, study the electronic relaxation owing to the reaction field, when no reoptimization is performed. Discuss the new charge distribution. The experimental volume of formamide is 65.990 A**3.

3) With the spherical cavity model, reoptimize the geometry of the formamide molecule, so the nuclear relaxation owing to solvent effect may be studied. Discuss again the charge distribution obtained.

REFERENCES

1) J. Bertran, A. Oliva, D. Rinaldi, J.L.Rivail, Nouv. J. Chimie, 4, 209 (1980)

2) D. Rinaldi, Computers and Chemistry, 1, 108(1976)

3) Program GEOMO, QCPE No. 290.

4) E. Sanchez Marcos, J. Maraver, M. F. Ruiz-Lopez and J. Bertran, Can. J. Chem., 2353, 64(1986)

Problem 14

The site of attack of benzene derivatives by nucleophiles or electrophiles has been interpreted through two static indexes: the charge index if the reaction is charge-controlled, and the frontier orbitals if the reaction if orbital-controlled. Most experimental data refer to studies in solution, sp charges and frontier orbitals may be dramatically altered by the presence of the solvent. Moreover, given the different charge distribution of the orto, meta and para adducts, the solvation energy in each of them can be also very different.

The goal of this problem is to study which factors determine the relative reactivity order when the reaction is carried out in solution. The benzonitryle molecule is taken as an example of benzene derivative. The semiempirical MNDO method will be used thoroughout.

Suggested Plan of Attack

---1---

a) Optimize the benzonitryle geometry and analyze the obtained static indexes.

b) Study in gas-phase: Entry of H+ and H- at the orto, meta, and para positions (minimization of intermediates only). Analyze the relative reactivity order, and discuss versus charge indexes and frontier orbitals of benzonitryle.

a) With the ellipsoidal cavity to model the solvent, and using the experimental volume of 169.528 A**3, carry out new energy calculations on optimized gas-phase neutral geometries. Use water as solvent (dielectric constant 78). Analyze new dipole moments, charge distribution and frontier orbitals.

b) Also by means of the ellipsoidal cavity model for the solvent, study the intermediates optimized in the gas phase with H+ or H- under solvent effect. Analyze the relative order of energies between the three isomers. Compare with gas-phase results, and discuss the influence of the solvation energy.

REFERENCES

1) J. Bertran, A. Oliva, D. Rinaldi, J.L.Rivail, Nouv. J. Chimie, 4, 209 (1980)

2) D. Rinaldi, Computers and Chemistry, 1, 108(1976)

3) Program GEOMO, QCPE No. 290.

4) E. Sanchez Marcos, J. Maraver, M. F. Ruiz-Lopez and J. Bertran, Can. J. Chem., 2353, 64(1986)

Problem 15

Influence of solvent on the Walden inversion reaction.

In this psoblem the solvent effect on the Walden Inversion Reaction on the (FCH3F)- system will be studied. The semiempirical AM1 method will be used for that purpose. Experimentally the inversion barrier in solution is about 25 kcal/mol. When theoretical calculations are carried out on the gas-phase reaction, a double-well profile appears. The purpose of this study is to determine the reaction profile in solution. Two ways to represent the solvent will be used: a discrete one, where each fluorine atom is attached to one water molecule, and a continuum one, where the (FCH3F)- system is placed into a cavity opened in the solute.

Suggested plan of attack:

Gas-phase:

1) Optimize at the AM1 level the gas-phase reactants.

2) Locate a possible intermediate for the F(-)...CH3F complex.

3) Locate the transition state of the reaction. This can be accomplished in two ways: a) by means of the AMPAC program, the SIGMA keyword (minimization of the gradient norm) can be used. b) The GEOMO program can be used, where the two F-C distances can be made the same by symmetry, and the hydrogens may be forced to be perpendicular to the F-C-F axis.

4) Get the force constants and vibrational modes for all species.

Discrete representation for the solvent:

5-8) Repeat steps 1-4 but with one water molecule attached to each fluorine. The O-H-F angle must always be forced to be linear or quasi-linear.

Continuum representation for the solvent:

The GEOMO program will be used necessarily in this step. The volumes (in angstrom**3) of the spherical cavities for each species are: , F-, 33.593; CH3F, 108.366; INT, 131.699, and TS 158.117. The volumes for reactants have been obtained from experimental data. For the intermediate and the transition state, they have been obtained though extrpolation from the Claussius-Mossoti relation between polarizabilities and volume.

9) Compute the solvation energy for each species with solvent dielectric constant 78 (i.e., for water). Construct new energy profile.

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1) J. Bertran, A. Oliva, D. Rinaldi, J.L.Rivail, Nouv. J. Chimie, 4, 209 (1980)

2) D. Rinaldi, Computers and Chemistry, 1, 108(1976)

3) Program GEOMO, QCPE No. 290.

Problem 16

Application of variational transition state theory to

$OH + H2 \longrightarrow H2O + H$ with harmonic approximation.

Conventional Transition State Theory (TST) may be interpreted as a calculation of the free energy of activation under the assumption that a configuration space dividing surface, located at the highest-potential-energy point (Saddle point) on the minimum-potential-energy path (MEP), provides a perfect bottleneck to reaction, i.e., that recrossing effects are negligible for such a dividing surface. Because recrossing usually occurs, TST rate constant will overestimate the exact classical result. To improve TST, in Canonical Variational Transition State Theory (CVT) location of the configuration-space dividing surface or Generalized Transition State (GTS), through which the equilibrium flux in the product direction is calculated, is optimized variationally as a function of the location s where it intersects the MEP, in order to obtain the minimum rate constant at a given Temperature. So, CVT locates Canonical Variational Transition State at the highest-free- energy-of-activation point on the MEP. A threshold-corrected version of CVT is called Improved Canonical Variational Theory (ICVT).

In this problem with the POLYRATE program, one will apply CVT and ICVT to the reaction $OH + H2 \longrightarrow H2O + H$, using the analytic potential energy surface obtained by Schatz and Elgersma by a fit to the ab initio calculations of Walch and Dunnning. Vibrational modes of the reactants, products and GTS are assumed to be harmonic.

Suggested plan of attack

1) Make a normal mode analysis of reactants, products and saddle point.

2) Construct the MEP and draw several geometries of the supermolecule along MEP.

3) Represent the classical potential energy (VMEP), the zero-point energy and the vibrationally adiabatic ground-state potential energy (VA) as functions of the distance (s) along the MEP from the saddle point. Locate the maximum value of VA.

4) Make a vibrational-mode correlation analysis along s : plot the frequencies versus s for the various nornal modes and identify the character of each mode as fuction of s.

5) Represent $\Delta G^{6T,0}$ (CVT) and $\Delta G^{6T,0}$ (ICVT) versus s at several Temperatures (T).

6) Find the Canonical Variational and the Improved Canonical Variational Transition States at different T.

7) Calculate the transmission coefficients by several ways, in order to model the quantal effects on reaction-coordinate motion at several T.

8) Calculate TST, CVT and ICVT forward and reverse rate constants at several T. Compare the obtained values with the experimental data:

T(K)	k(cm3 Molecule-1 seg-1)
298	6.08 + 0.37 E-15
400	3.7 + 1.1 E-14
600	2.9 + 0.9 E-13
1000	2.4 + 0.7 E-12

9) Calculate the Equilibrum Constants.

10) Make a factor ratio analysis of CVT and TST rate constants.

11) Make a global discussion of results.

Problem 17

Application of variational transition state theory to

$OH + H2 \longrightarrow H2O + H$ With inclusion of anharmonicity

In general, the vibrational degrees of freedom of the reactants, products and GTS are bound by an anharmonic potential which contains terms in normal coordinates of order higher than two. Substantial differences can be obtained between rate constants computed from harmonic and anharmonic vibrations. In this problem, one will study the reaction $OH + H2 \longrightarrow H2O + H$ with anharmonicity modeled by the Morse I- quadratic-quartic approximation.

Suggested plan of attack

Repeat the preceding problem including now the anharmonicity. Take into account that it is not necessary to calculate again each step because a lot of results are invariant upon introduction of anharmonicity. Compare the results obtained in both cases.

Problem 18

Application of the statistical-diabatic model for state-selected reaction rates to

$$OH\ (nOH) + H2\ (nHH) \longrightarrow H2O + H\ .$$

In this problem a vibrationally diabatic version of Variational Transition State Theory is employed to calculate the rate constants k(nOH ,nHH ,T) for the vibrational-state-selected reaction $OH\ (nOH) + H2\ (nHH) \longrightarrow H2O + H$, where the rotational and traslational degrees of freedom are at Temperature T . The experimental results have shown that excitation of the bond to be broken (H2) has a large effect on the rate constant and excitation of the spectator (O-H) bond has a small effect.

The Schatz-Elgersma analytic potential energy surface is used and the Morse I quadratic-quartic approximation for anharmonicity is adopted.

Suggested plan of attack

Repeat the steps 3,5,6,7,8,9,10 and 11 of the problem 16, for the three following cases:

A) nOH = 0 nHH = 0

B) nOH = 1 nHH = 0

C) nOH = 0 nHH = 1

Compare each case with the completely thermally averaged reaction rates.

List of references for Problems 16,17, and 18.

[1] D.G. Truhlar, A.D. Isaacson and B.C. Garrett, "Theory of Chemical Reaction Dynamics", Vol. IV, M. Baer, Ed., CRC Press, Boca Raton, FL, 1985.

[2] A.D. Isaacson, D.G. Truhlar, S.N. Rai, R. Steckler, G.C. Hancock, B.C. Garrett and M.J. Redmon, Comp. Phys. Comm, 47, 91 (1987).

[3] W.H. Miller, N.C. Handy and J.E. Adams, J. Chem. Phys., 72, 99 (1980).

[4] G.C. Schatz and H. Elgersma, Chem. Phys. Lett., 73, 21 (1980).

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[6] A.D. Isaacson and D.G. Truhlar, J. Chem. Phys., 76, 1380 (1982).

[7] D.G. Truhlar and A.D. Isaacson, J. Chem. Phys., 77, 3516 (1982).

[8] A.D. Isaacson, M.T. Sund, S.N. Rai and D.G. Truhlar, J. Chem. Phys., 82, 1338 (1985).