

Electronic and Structural Properties of Model S_N2 Reactions

by

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To my parents
and
my husband

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Abstract

The properties of the electronic charge distribution are used to study the electronic structures, reactivities and intrinsic barriers of some model S_N2 reactions. Computations were carried out at the Hartree-Fock and second-order Møller-Plesset (MP2) levels. The systems examined are $N^- + CH_3X \rightarrow CH_3N + X^-$, where N and X are H, CCH, $\underline{CN}$, $\underline{NC}$, NH_2 , OH, OOH, F, PH_2 , SH and Cl. Using the integrated charges obtained from the molecular structure theory, a way of analysing the electronic structure of the transition state is proposed and is used to study the electronic structures of model S_N2 reactions. Results at the MP2 level show that for asymmetric reactions, the reactant and product do not make equal contributions to the transition state wavefunction. However, in some of the reactions, valence-bond configurations $N^- \cdot R \cdot X$ and $N \cdot R \cdot X^-$, which are constituents of the reactant and product wavefunctions, respectively, make similar contributions to the transition state. Thus, in these reactions N and X do have equal charges at the transition state. The charge development on the leaving group is related not only to the exothermicity of the reaction but also to the electronic structure of the transition state and to the electronegativity of the leaving group. The factors determining the height of the intrinsic barrier are discussed. For symmetric reactions, the type of C-X bonding affects the barrier significantly. Within the same type of reaction, the intrinsic barrier is related to the electronegativity of the X group. The Laplacian of the charge density is used to study the shell structures of free atoms and also the different reaction processes of nucleophilic substitution at carbon and at silicon. It is shown that electronegativity and polarizability play an important role in the reaction process. The stereochemistry of silicon is explained by the Laplacian of the charge density.

List of Symbols

Symbol	Meaning
$\hbar$	Planck's constant divided by 2π
m	mass of an electron
e	charge of an electron
Z	charge of a nucleus
M	mass of a nucleus
ρ	charge density
$\nabla\rho$	gradient of the charge density
$\nabla^2\rho$	the Laplacian of the charge density
$\Delta E_c(I)$	energy change upon the formation of the reactant ion-molecule complex from reactant
$\Delta E_c(II)$	energy change upon the formation of the product ion-molecule complex from product
ΔE_c^b	energy barrier for the second step of the reaction
ΔE_c°	energy change for the second step of the reaction
ΔE^b	energy barrier for the entire reaction
ΔE_t°	energy change for the entire reaction
R_{A-B}	bond length between atoms A and B
r_{C-A}	distance between bond critical point and atom A

Q_A	net charge on A
ΔQ_A	charge development on A
$\Delta E^\ddagger$	potential energy barrier
ΔE°	intrinsic barrier
ΔE°	elementary reaction energy
R_α	TS bond length change parameter
$D(r)$	radial density function
r_i	radius of the i th minimum in $\nabla^2\rho$
$r_{\min}$	radius of the outermost minimum in $\nabla^2\rho$
r_{odd}	radius of the outermost odd numbered zero of $\nabla^2\rho$
$r_{\max}$	radius of the outermost maximum in $\nabla^2\rho$
$\Delta(\nabla^2\rho)$	difference in $\nabla^2\rho$ values

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Chapter 1

Introduction

1.1 Overview

A fundamental postulate of quantum mechanics states that everything that can be known about a system is contained in the state function Ψ . This postulate has been used by Bader and coworkers to develop a molecular structure theory,¹ in which the gradient vector field and the scalar field of the electronic charge distribution $\rho(\mathbf{r})$ are used to study the bonds, atomic interactions, reactivities and stabilities of molecular systems.

According to the theory, the properties of the gradient vector field $\nabla\rho(\mathbf{r})$ provide a definition of the elements of molecular structure. Thus, the molecular charge density is uniquely partitioned into atoms bounded by the zero-flux surfaces in $\nabla\rho(\mathbf{r})$ and chemical bonds are manifested by the existence of bond paths in the gradient vector field of $\nabla\rho(\mathbf{r})$. Furthermore, the network of bonds linking the atoms in a molecule enables one to assign a structure and to determine whether or not the structure is stable. On the other hand, the properties of the scalar field of the charge density, the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, provide an understanding of atomic interactions and the reactivity of a molecule. As noted by Morse and Feshbach,² the Laplacian is an extremely important property of a scalar field. In particular, the Laplacian of the charge density identifies the regions of space wherein the electronic charge of a molecule is locally concentrated or depleted.

Moreover, an expression derived from the quantum mechanical stress tensor relates the sign of the Laplacian of ρ to the relative magnitudes of the local contribution of the potential and kinetic energy density to their virial theorem average.

Studies on molecular systems using the properties of $\nabla\rho(r)$ and $\nabla^2\rho(r)$ show that bonds can be characterized in terms of the properties of the bond path and of ρ at the bond critical point.³ The ellipticity of the bond provides a measure of the extent to which charge is preferentially accumulated in a given plane. Also the Laplacian of the charge density demonstrates the existence of a local concentration of electronic charge in both the bonded and nonbonded regions of an atom in a molecule. The numbers, locations and relative sizes of the bonded and nonbonded concentrations of charge in the valence shell of a bonded atom, as determined by the Laplacian of ρ , agree in general with the corresponding VSEPR model.⁴ Furthermore, it has been found that the regions of charge concentration and charge depletion in the Laplacian distribution coincide with the regions of space where the HOMO (the highest occupied molecular orbital) and the LUMO (the lowest unoccupied molecular orbital), respectively, are most concentrated.⁵ Also, the regions of maximum electronic charge concentration and depletion, as determined by the Laplacian of ρ , correlate with the positions of electrophilic and nucleophilic attack,^{4b,5,6} respectively.

The properties of the electronic charge density provide an attractive tool for the study of atomic and molecular systems. In this thesis the properties of the electronic charge density are used to study the structures of atoms and to study some model S_N2 reactions, with the aim

of providing further insight into the electronic structures of the transition states of the reactions. A second goal is to provide a deeper understanding of intrinsic barriers and the reactivities of the model systems.

Transition state studies of model S_N2 reactions $N^- + CH_3X \rightarrow X^- + CH_3N$ where N and X are H, CCH, $\underline{CN}$, $\underline{NC}$, NH_2 , OH, OOH, F, PH_2 , SH and Cl are reported in chapter 3. In chapter 4, intrinsic barriers of model reactions and the rate-equilibrium relationship are discussed. In chapter 5, the Laplacian of the charge density is used to study the electronic structures of the free atoms Li to Xe and electronegativities. Furthermore, the Laplacian of the charge density is used to study the reactivity and stereochemistry of nucleophilic substitution reactions at carbon and silicon.

1.2 Gradient Vector Field of the Charge Density ($\nabla\rho$)

For a fixed configuration of nuclei, the charge distribution for a system containing N electrons is defined by

$$\rho(\mathbf{r}) = N \sum_{\text{spin}} \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) d\mathbf{r}_2, \dots, d\mathbf{r}_n \quad (1.2.1)$$

where Ψ is a properly antisymmetrized solution to the general time-independent Schrödinger equation, $\mathbf{x}_i$ is a combination of the space and spin coordinates of the i th electron and $\mathbf{r}_i$ denotes the space coordinates of the i th electron.

For a given nuclear configuration, the topological properties of ρ are faithfully mapped out by the associated gradient vector field of the

charge density, $\nabla\rho$. As an example, the gradient vector field of the water molecule is illustrated in Fig. 1.2.1. In this vector field, the vector $\nabla\rho$ points in the direction of maximum increase in ρ and a gradient path is generated by following the path traced out by a succession of such vectors starting at some initial point. A gradient path is orthogonal to a contour of constant ρ at any of its points.

The essential topological properties of ρ can be summarized by the complete specification of its critical points at which $\nabla\rho = 0$. A critical point, denoted by $\mathbf{r}_c$, is classified according to its rank and signature (λ, σ) .^{1a,7} The rank λ of a critical point equals the number of non-zero eigenvalues of the Hessian matrix of $\rho(\mathbf{r}_c)$, $H(\rho) = [H_{ij}(\rho)]$, while the signature σ is the algebraic sum of the signs of the eigenvalues.

The Hessian matrix of $\rho(\mathbf{r})$ is the matrix of second derivatives of $\rho(\mathbf{r})$ with respect to the position coordinates

$$H_{ij}(\rho) = \left[\frac{\partial^2 \rho}{\partial r_i \partial r_j} \right]_{\mathbf{r} = \mathbf{r}_c} \quad (1.2.2)$$

There can be two types of critical points: a nondegenerate or rank-three critical point with

$$\det | H(\rho) |_{\mathbf{r} = \mathbf{r}_c} \neq 0 \quad (1.2.3)$$

and a degenerate critical point, for which $\det | H(\rho) |$ vanishes, since $H(\rho)$ is of rank less than three at such a point.

The eigenvalues of $H(\rho)$ at each critical point indicate the

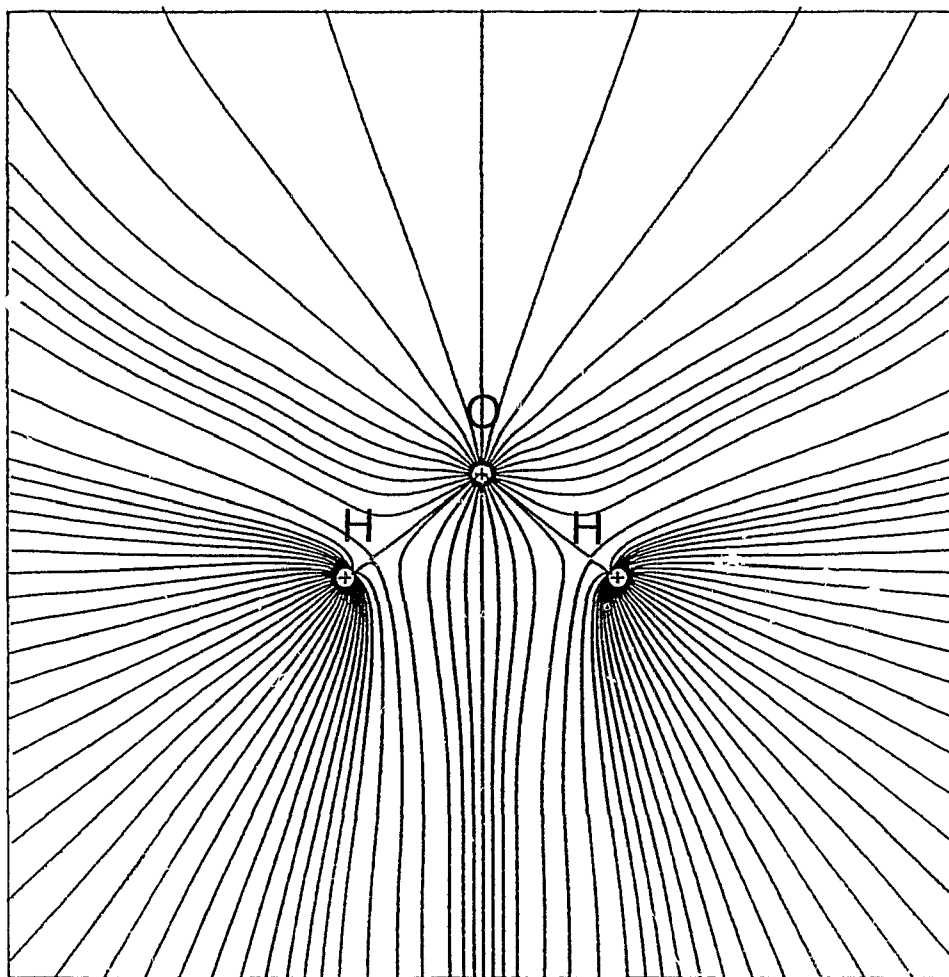


Figure 1.2.1 Gradient vector field of the H_2O molecule.

curvatures of $\rho(r_c)$ and determine the three orthogonal eigenvectors of gradient paths which either terminate or originate at the critical point. If the eigenvalue is positive its associated eigenvector or gradient path originates at the critical point and is directed away from the critical point. If the eigenvalue is negative, the associated gradient path terminates at the critical point and is directed toward the critical point, see Fig. 1.2.2.

In the case of a nondegenerate critical point, four types of critical point are possible, i.e., (3,-3), (3,+3), (3,+1) and (3,-1).

A (3,-3) critical point has three negative eigenvalues of the Hessian matrix, corresponding to three negative curvatures. Hence, it is a local maximum in ρ and also all gradient paths in the vicinity of the critical point terminate at this critical point. A (3,-3) critical point exhibits the properties which define an attractor of the gradient vector field of the charge distribution. For a ground state system, a (3,-3) critical point exists only at nuclei (non-nuclear maxima have been found in the charge distribution of Li and Na clusters and may be typical of the alkali metals).^{7b,8} Due to the nuclear coalescence cusp condition on the state function and hence on the charge density, $\nabla\rho(r)$ is undefined at a nucleus. Consequently the maximum in $\rho(r)$ at the position of a nucleus is not a true critical point, as $\nabla\rho(r)$ does not vanish. However, the topological behaviour of $\rho(r)$ in the region of a nuclear cusp is the same as if it were a true (3,-3) critical point.^{1a,8a}

A local minimum in $\rho(r)$ has three positive curvatures, each associated with a positive eigenvalue. Such a minimum corresponds to a (3,+3) critical point and is observed in a cage structure. These

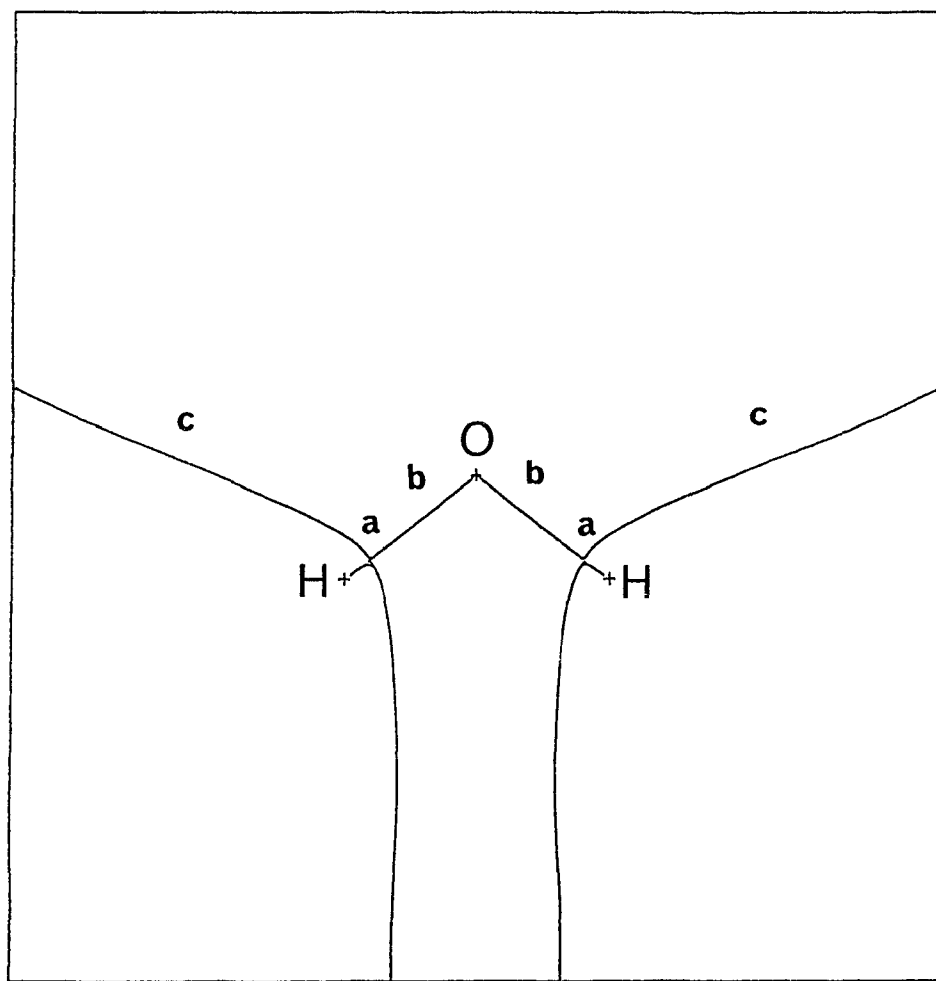


Figure 1.2.2 Molecular graph of the H_2O molecule.

- a) bond critical point;
- b) bond path;
- c) interatomic surface.

critical points are also known as cage critical points.

A (3,+1) critical point is a saddle point which has two positive eigenvalues and one negative eigenvalue. Motion along the unique axis, associated with the negative eigenvalue, towards the critical point leads to an increase in $\rho(r)$. A (3,+1) critical point can be found in a ring structure and therefore is called a ring critical point.

A (3,-1) critical point has two negative and one positive eigenvalues. The two eigenvectors associated with the negative eigenvalues define a surface on which the critical point is a local maximum. The eigenvector associated with the positive eigenvalue defines a unique axis along which the charge density decreases for motion towards the critical point. The value of $\rho(r_c)$ is the local minimum along this axis. A (3,-1) critical point appears between every pair of neighboring bonded atoms and is therefore called a bond critical point.

For a system with a finite number of nuclei, the number of (3,-3) critical points (n_{-3}), (3,+3) critical points (n_{+3}), (3,+1) critical points (n_{+1}) and (3,-1) critical points (n_{-1}) are related by eq. (1.2.4)^{1a,7b,8a}

$$n_{-3} - n_{+3} + n_{+1} - n_{-1} = 1 \quad (1.2.4)$$

With information on the gradient vector field and the critical points of ρ at hand, the definitions of bonds and interatomic surfaces can be made immediately. The necessary and sufficient condition for the existence of a bond is the existence of a bond path. The bond path is a pair of gradient paths which originate at a (3,-1) critical point and

terminate at neighboring nuclei.^{1a,7b,9} It is defined by the eigenvector associated with the unique positive eigenvalue of a (3,-1) critical point. A bond path is a line through the charge density along which $\rho(r)$ is a maximum with respect to any lateral displacement, see Fig. 1.2.2.

The network of bond paths defines the molecular graph of a molecule,^{1a,7b} The set of molecular graphs which contain the same number of bond paths linking the same nuclei define a molecular structure^{1a,7b}. For a molecular structure to be stable, it must satisfy two requirements: a) every critical point in ρ must be nondegenerate i.e. have three non-zero eigenvalues; b) the critical points of a charge distribution are linked by trajectories of $\nabla\rho$.^{1a,9}

The gradient paths defined by the eigenvectors associated with the negative eigenvalues of the Hessian matrix of a (3,-1) critical point generate an interatomic surface. The interatomic surface and the surfaces at infinity are the only closed surfaces which satisfy the equation^{8a,10}

$$\nabla\rho(r) \cdot n(r) = 0 \quad \forall r \in s \quad (1.2.5)$$

where $n(r)$ is the unit vector normal to the surface at r . A surface that satisfies this equation is known as "a zero-flux surface" since there is no flux in $\nabla\rho$ through the surface. An atom is defined by a real space surrounded by a zero-flux surface.^{8a,10} This definition of an atom is not only unique, but as we will see later, the virial relationship is followed.

By appealing to quantum mechanics,^{1b} one finds that the zero-flux

surface condition (eq. (1.2.5)) leads to a variational definition of its average properties. One consequence of this definition is that any atomic property F is the average over the atomic basin of an effective single-particle density $f(\mathbf{r})$. Thus the value of the property F for atom Ω is

$$F(\Omega) = \int_{\Omega} f(\mathbf{r}) \, d\mathbf{r} \quad (1.2.6)$$

It follows from this definition that the average value of F for a total molecular system is given by the sum over the atoms in the molecule of the corresponding atomic values.

$$F = \sum_{\Omega} F(\Omega) \quad (1.2.7)$$

The atomic charge of an atom is obtained by integrating ρ over the basin of the atom to obtain its average electron population $N(\Omega)$ followed by the subtraction of this average electron population from the nuclear charge Z_{Ω}

$$Q(\Omega) = Z_{\Omega} - \int_{\Omega} \rho(\mathbf{r}) \, d\mathbf{r} = Z_{\Omega} - N(\Omega) \quad (1.2.8)$$

Kinetic energy is obtained by integrating the local kinetic energy over the basin of an atom,

$$K(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla \nabla \Gamma(\mathbf{r}, \mathbf{r}')_{\mathbf{r}=\mathbf{r}'} \quad (1.2.9)$$

$$G(\mathbf{r}) = \frac{\hbar^2}{2m} \nabla \cdot \nabla' \Gamma(\mathbf{r}, \mathbf{r}')_{\mathbf{r}=\mathbf{r}'} \quad (1.2.10)$$

$\Gamma(\mathbf{r}, \mathbf{r}')$ is the one-electron spinless density matrix¹¹

$$\Gamma(\mathbf{r}, \mathbf{r}') = N \sum_{\text{spin}} \int \Psi^* (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \Psi (\mathbf{x}_1', \mathbf{x}_2, \dots, \mathbf{x}_n) d\mathbf{r}_2, \dots, d\mathbf{r}_n \quad (1.2.11)$$

These two kinetic densities yield the same average kinetic energy of an atom

$$K(\Omega) = \int_{\Omega} K(\mathbf{r}) d\mathbf{r} = \int_{\Omega} G(\mathbf{r}) d\mathbf{r} \quad (1.2.12)$$

This follows from the fact¹² that

$$K(\mathbf{r}) = L(\mathbf{r}) + G(\mathbf{r}) \quad (1.2.13)$$

$$L(\mathbf{r}) = - \frac{\hbar^2}{4m} \nabla^2 \rho(\mathbf{r}) \quad (1.2.14)$$

$$L(\Omega) = \int_{\Omega} L(\mathbf{r}) d\mathbf{r} \quad (1.2.15)$$

$$= - \frac{\hbar^2}{4m} \int_{\Omega} \nabla^2 \rho(\mathbf{r}) d\mathbf{r}$$

$$= - \frac{\hbar^2}{4m} \oint_S \nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) d\mathbf{s}(\mathbf{r})$$

and from the definition of an interatomic surface, eq. (1.2.5), $L(\Omega)=0$.

1.3 The Scalar Field of the Charge Density ($\nabla^2 \rho$)

The Laplacian of the charge density is defined as the sum of the three principal curvatures of the function at each point in space, that is^{2,10}

$$\nabla^2 \rho(\mathbf{r}) = \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2} \quad (1.3.1)$$

In one dimension, the curvature of $\rho(x)$ is a measure of the difference between the average value of ρ at points neighboring x and its value at x . This follows from the fundamental definition of the derivative²

$$\begin{aligned} & \lim \left\{ \rho(x) - \frac{1}{2} [\rho(x-dx) + \rho(x+dx)] \right\} \\ &= -\frac{1}{2} \lim \left\{ [\rho(x+dx) - \rho(x)] - [\rho(x) - \rho(x-dx)] \right\} \\ &= -\frac{1}{2} \left[\frac{d^2 \rho}{dx^2} \right] (dx^2) \end{aligned} \quad (1.3.2)$$

When $\nabla^2 \rho(x) < 0$, ρ at x is larger than the average of ρ at $x+dx$ and $x-dx$ and ρ will have a downward curvature at that point when plotted against x . Similarly when $\nabla^2 \rho(x) > 0$, ρ at x is less than its average value at neighboring points. Similarly, in three dimensions, when $\nabla^2 \rho(\mathbf{r}) < 0$, then the ρ at point $\mathbf{r}$ is greater than its average value at neighboring points and when $\nabla^2 \rho(\mathbf{r}) > 0$, the value of ρ at $\mathbf{r}$ is less than its average value at neighboring points. Thus a minimum in $\nabla^2 \rho(\mathbf{r})$ with a negative value means that the electronic charge is locally concentrated in that region of space, even though the charge density itself exhibits no corresponding maximum. This property of $\nabla^2 \rho(\mathbf{r})$ must be distinguished from local maxima and minima in $\rho(\mathbf{r})$. An example of a Laplacian of ρ

plot for a molecule is shown in Fig. 1.3.1.

The Laplacian of the charge density is directly related to the local contributions to the electronic energy of a system via the equation^{2,3}

$$\frac{\hbar^2}{4m} \nabla^2 \rho(\mathbf{r}) = V(\mathbf{r}) + 2G(\mathbf{r}) \quad (1.3.3)$$

where $V(\mathbf{r})$ is the potential energy density as defined in eq. (1.3.4) and $G(\mathbf{r})$ is the kinetic energy density as defined in eq. (1.2.10)

$$V(\mathbf{r}) = \{ -\mathbf{r} \cdot \nabla \cdot \vec{\sigma}(\mathbf{r}) + \nabla \cdot [\mathbf{r} \cdot \vec{\sigma}(\mathbf{r})] \} \quad (1.3.4)$$

$\vec{\sigma}(\mathbf{r})$ is the stress tensor defined by

$$\vec{\sigma}(\mathbf{r}) = \frac{\hbar^2}{4m} \{ (\nabla \nabla + \nabla' \nabla') - (\nabla \nabla' + \nabla' \nabla) \} \Gamma(\mathbf{r}, \mathbf{r}') \big|_{\mathbf{r} = \mathbf{r}'} \quad (1.3.5)$$

Integration of the potential density over an atomic basin yields the average electronic potential energy of the atom. As the integral of the Laplacian of ρ vanishes over an atomic basin (eq. 1.2.15), integration of eq. (1.3.3) over an atom yields

$$V(\Omega) + 2T(\Omega) = \int_{\Omega} V(\mathbf{r}) d\mathbf{r} + 2 \int_{\Omega} G(\mathbf{r}) d\mathbf{r} = \frac{\hbar^2}{4m} \int_{\Omega} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = 0 \quad (1.3.6)$$

which is the same as for the total system, i.e. $V + 2T = 0$. Thus eq. (1.3.3) is the local expression for the virial theorem.

Since the potential and kinetic energy density are everywhere negative and positive respectively, the sign of the Laplacian of the

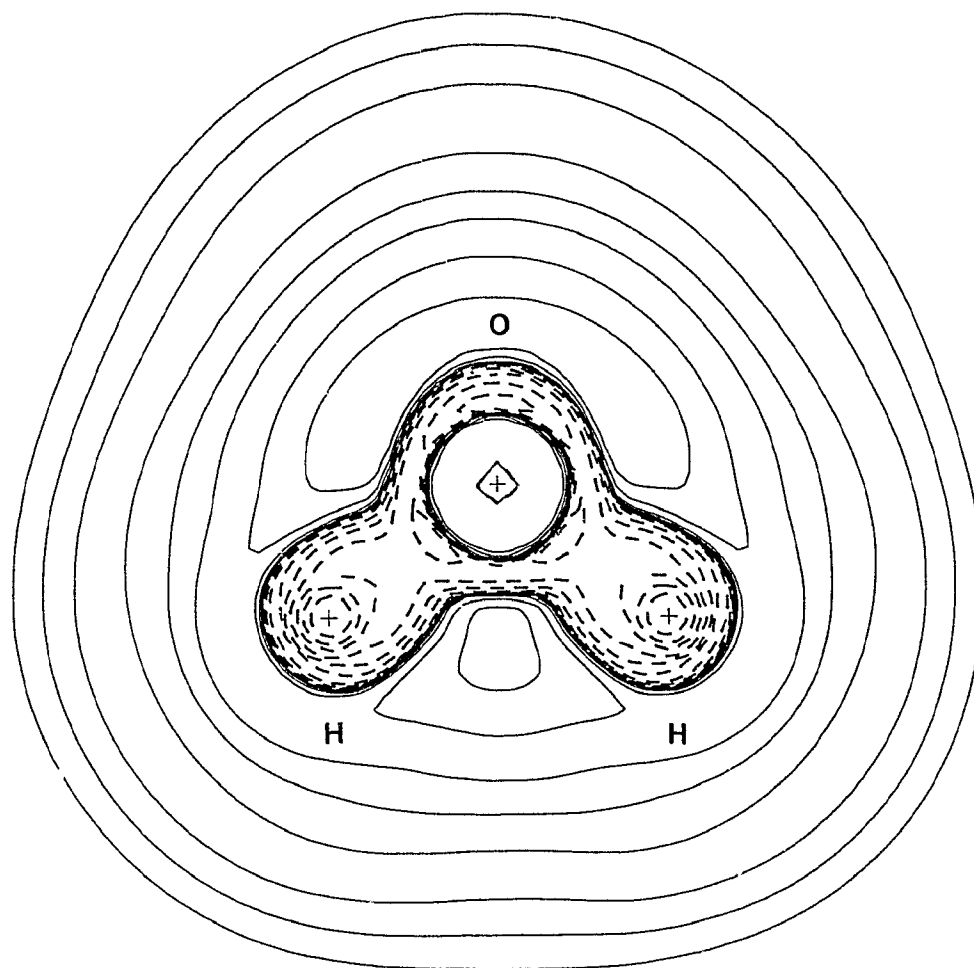


Figure 1.3.1 The Laplacian of $\rho(\mathbf{r})$ in the molecular plane of H_2O .

charge density determines which of the two contributions to the total energy is in excess over their virial average $|V(\Omega)/T(\Omega)| = 2$. In regions of space where the Laplacian is negative and electronic charge is concentrated, the potential energy dominates both the local total energy $E(\mathbf{r}) = V(\mathbf{r}) + G(\mathbf{r})$ and the local virial relationship. In general, the more negative the value of the Laplacian over some region of space, the greater is the contribution of the electronic charge in that region to the total energy of the system. Furthermore, as a consequence of the vanishing of the integral of the Laplacian of ρ over a system or a subsystem bounded by a zero-flux surface, there is a constraint on the relative extents of concentration and depletion of charge, i.e. if charge is concentrated in some regions of an atom, it must be depleted to a corresponding extent in other regions.

Chapter 2

Theoretical Methods

2.1 Hartree-Fock Method

For a system of N electrons and M nuclei, the time-independent Schrödinger equation is

$$H \Phi = E \Phi \quad (2.1.1)$$

where H is the molecular Hamiltonian operator, Φ is a state function in Hilbert space $\mathcal{H}$, which completely defines the dynamical state of the system, and E is an allowed energy value. Within the framework of non-relativistic quantum mechanics, the total molecular Hamiltonian takes the form

$$H = T_n + T_e + V_n + V_e + V_{ne} \quad (2.1.2)$$

with nuclear kinetic energy operator

$$T_n = -\frac{\hbar^2}{2} \sum_A \frac{1}{M_A} \nabla_A^2 \quad (2.1.3)$$

where M_A is the mass of nucleus A . The electronic kinetic energy operator is

$$T_e = -\frac{\hbar^2}{2m} \sum_p^N \nabla_p^2 \quad (2.1.4)$$

and the nucleus-nucleus repulsion term is

$$V_n = \sum_{A < B}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.1.5)$$

where Z_A is the charge on nucleus A. The electron-electron repulsion term is

$$V_e = \sum_{p < q}^N \frac{e^2}{r_{pq}} \quad (2.1.6)$$

and the electron-nucleus attraction term is

$$V_{ne} = - \sum_p^N \sum_A^M \frac{Z_A e}{r_{pA}} \quad (2.1.7)$$

The Schrödinger equation (2.1.1) is a second-order differential equation in $3(N + M)$ variables. The solution of the equation is no simple matter and can only be obtained by resorting to various approximations. Invariably, the first approximation invoked is the Born-Oppenheimer approximation. Born and Oppenheimer's mathematical treatment showed that¹³ the true molecular wavefunction is adequately approximated as

$$\Phi(r, R) \approx \Psi_e(r; R) \Psi_n(R) \quad (2.1.8)$$

if

$$\left(\frac{m}{M}\right)^{1/4} \ll 1$$

where Ψ_e is an electronic wavefunction and Ψ_n is a nuclear wavefunction. Physically, it is expected that the disparity of the mass of the electron and the mass of the nuclei in a molecule will lead to electronic and nuclear motions at dramatically different speeds and therefore the electrons can respond almost instantaneously to any change in the position of the nuclei. Consequently, the electronic and nuclear motion can be treated separately to a very good approximation. Thus, eq. (2.1.1) can be separated into two equations

$$H_e(r;R) \Psi_e(r;R) = E_e(R) \Psi_e(r;R) \quad (2.1.9)$$

and

$$H_n(R) \Psi_n(R) = E \Psi_n(R) \quad (2.1.10)$$

where H_e is the electronic Hamiltonian of the form

$$H_e(r;R) = T_e(r) + V_e(r) + V_{ne}(r;R) \quad (2.1.11)$$

and H_n has the form

$$H_n(R) = T_n(R) + V_n(R) + E_e(R) \quad (2.1.12)$$

Eq. (2.1.9) depends on the electronic coordinates at a fixed position R of the nuclei and yields as solution the electronic wavefunction Ψ_e and electronic energy E_e for a given nuclear arrangement. Eq (2.1.10)

describes the nuclear motion in the potential

$$U(R) = V_n(R) + E_e(R) \quad (2.1.13)$$

Hence, in order to obtain the potential energy surface $U(R)$, one has to solve the electronic Schrödinger equation (2.1.9) for a number of nuclear positions. The further term $V_n(R)$ is easily evaluated. Eq. (2.1.10) can be solved without much problem.¹⁴ Thus the most difficult part of all molecular calculations is to solve the electronic Schrödinger equation (2.1.9). From now on, as we only consider the solution of the electronic Schrödinger equation, the subscript "e" is dropped.

The electronic Schrödinger equation (2.1.9) is a many-electron problem whose solution is normally obtained within the independent electron model. The most widely used form of the independent electron model is the Hartree-Fock model.

The essence of the Hartree-Fock approximation¹⁵ is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way. The electronic wavefunction is represented by a single determinant of the products of single-electron spin orbitals eq (2.1.14), in which the orbitals are

$$\Psi_0 = (N!)^{-1/2} |\chi_1 \chi_2 \cdots \chi_N| \quad (2.1.14)$$

optimized according to the variation principle, such that the electronic energy

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \quad (2.1.15)$$

is minimized. In doing so, one obtains an equation that defines the best spin orbitals, the one that minimize E_0 . This equation for the best spin orbitals is the Hartree-Fock integro-differential equation

$$f \chi_i = \epsilon_i \chi_i \quad (2.1.16)$$

where f is an effective one-electron operator, called the Fock operator, of the form

$$f(p) = h(p) + v_{(p)}^{HF} \quad (2.1.17)$$

$h(p)$ is a core-Hamiltonian operator which in atomic units takes the form (from now on, atomic units are used exclusively in this chapter unless otherwise indicated)

$$h(p) = -\frac{1}{2} \nabla_p^2 - \sum_A \frac{Z_A}{r_{pA}} \quad (2.1.18)$$

$v_{(p)}^{HF}$, the average potential experienced by electron p due to the presence of the other electrons, has the form

$$v_{(p)}^{HF} = \sum_j^N [J_j(p) - K_j(p)] \quad (2.1.19)$$

where $J_j(p)$, the Coulomb operator, is given by

$$J_j(p) = \langle \chi_j(q) \mid \frac{1}{r_{pq}} \mid \chi_j(q) \rangle \quad (2.1.20)$$

and $K_j(p)$, the exchange operator, has the property

$$K_j(p) \chi_i(p) = \langle \chi_j(q) \mid \frac{1}{r_{pq}} \mid \chi_i(q) \rangle \cdot \chi_j(p) \quad (2.1.21)$$

The Hartree-Fock potential ν^{HF} or equivalently the "field" seen by electron p , depends on the spin orbitals of the other electrons (i.e. the Fock operator depends on its eigenfunctions). Thus the Hartree-Fock equations are nonlinear and must be solved iteratively. The procedure for solving the Hartree-Fock equations is called the self-consistent-field (SCF) method. The eigenvalue of the Fock operator ϵ_i is

$$\epsilon_i = h_i + \sum_j^N (J_{ij} - K_{ij}) \quad (2.1.22)$$

where

$$h_i = \langle \chi_i \mid h \mid \chi_i \rangle \quad (2.1.23)$$

$$J_{ij} = \langle \chi_i \mid J_j \mid \chi_i \rangle \quad (2.1.24)$$

$$K_{ij} = \langle \chi_i \mid K_j \mid \chi_i \rangle \quad (2.1.25)$$

and the total Hartree-Fock electronic energy E is

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \sum_i^N \sum_j^N (J_{ij} - K_{ij}) \quad (2.1.26)$$

Exact solutions to the Hartree-Fock equations (2.1.16) are only possible, in practice, for atoms where the spherical symmetry of the system permits reduction to a system of coupled one-dimensional equations (for diatomic molecules, numerical solutions have been recently reported¹⁶). For molecules, approximate solutions of the equation may be obtained by expanding all functions χ which arise in terms of some set of fixed basis functions. If the basis functions ϕ_r ($r = 1, 2, \dots \infty$) constitute a complete set, then any function may be expressed in the form

$$\chi = \sum_r c_r \phi_r \quad (2.1.27)$$

with negligible error by including sufficient terms in the expansion. By employing the basis set expansion technique, the problem of finding the best function χ is simplified to finding the best set of coefficients and the integro-differential equations are converted into matrix equations. If a sufficiently large number of terms are included in eq (2.1.27), results obtained by the expansion method tend to the exact solutions of the Hartree-Fock equations and are, of course, independent of the nature of the basis functions. In practice, it is often not feasible to include sufficient terms in the expansion for convergence to accurate Hartree-Fock solutions and the quality of the approximation equation (2.1.27) is then critically dependent on the choice of basis functions. Basis functions are discussed further in section 2.3.

Hartree-Fock calculations account for the majority of molecular calculations. The Hartree-Fock method is capable of recovering a large

fraction of the total energy of a system and also leads to expectation values of some one-electron properties which are of an acceptable accuracy. Furthermore, the Hartree-Fock method provides a simple orbital picture of electronic structure. The Hartree-Fock method does, however, have a number of deficiencies. The primary deficiency is the inadequate treatment of the correlation between motions of electrons. In particular, single-determinant wavefunctions take no account of correlation between electrons with opposite spin. Correlation of the motions of the electrons with the same spin is partially, but not completely accounted for by virtue of the determinantal form of the wavefunction. This results in quantitatively inadequate energies of chemical interest. Furthermore, the single-determinant wavefunction leads to a number of qualitatively incorrect descriptions of electronic structure. In fact, whenever two or more molecular states from different configurations have similar total energies and interact strongly, the Hartree-Fock method breaks down. To improve upon a Hartree-Fock calculation, the effects of electron correlation must be included. This will be the subject of the next section.

2.2 Møller-Plesset Perturbation Theory

Due to the limitations of the current computers, even with orbital expansion in a finite basis, a full configuration interaction calculation is only possible for small systems. A great deal of effort has been made to develop methods which are efficient and accurate enough to give an adequate approximation to the full configuration interaction result. The frequently used methods include limited configuration

interaction (CI), perturbation and coupled cluster methods.¹⁷

Møller-Plesset perturbation theory is based on many-body perturbation theory, in which, the Hartree-Fock operator H_0 is taken as the zero-order Hamiltonian^{17b}

$$H_0 = \sum_p^N f(p) \quad (2.2.1)$$

and the Hartree-Fock wavefunction is taken as the zero-order wavefunction

$$\Psi^{(0)} = \Psi_0 \quad (2.2.2)$$

The many-electronic Hamiltonian is written in the form

$$H = H_0 + V \quad (2.2.3)$$

where V is regarded as a small perturbation

$$V = H - H_0 \quad (2.2.4)$$

$$= \sum_{p < q} \frac{1}{r_{pq}} - v_{(p)}^{\text{HF}}$$

The exact eigenfunction Ψ , which is supposed to lie near the Hartree-Fock solution Ψ_0 and the exact eigenvalue E , which is supposed to lie near the corresponding E_0 , can be expressed in the following series

$$\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots \quad (2.2.5)$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots \quad (2.2.6)$$

where $\Psi^{(i)}$, $E^{(i)}$ are the i th-order correction to the wavefunction and energy, respectively. In practice, the expansion is truncated after finite order. The method is referred to by the highest order energy term allowed, that is, truncating after second-order energy as MP2, after third-order as MP3 and so forth.

The correction terms $\Psi^{(1)}$, $\Psi^{(2)}$, $\dots$ are developed in terms of the complete set of Hartree-Fock eigenfunctions Ψ_s ($s = 0, 1, 2, \dots$)

$$\Psi^{(1)} = \sum_s a_s^{(1)} \Psi_s \quad (2.2.7)$$

$$\Psi^{(2)} = \sum_s a_s^{(2)} \Psi_s \quad (2.2.8)$$

Ψ_s ($s = 0, 1, 2, \dots$) are single-determinants and may be classified (apart from $s = 0$ which has the lowest eigenvalue and is used as the reference configuration) as single substitutions $i \rightarrow a$, double substitutions $ij \rightarrow ab$, and so forth. $ij \rightarrow ab$ implies that χ_i is replaced by χ_a and χ_j by χ_b . Their corresponding eigenvalues are denoted as E_s

$$E_0 = \sum_i^N \epsilon_i \quad (2.2.9)$$

$$E_{i \rightarrow a} - E_0 = \epsilon_a - \epsilon_i \quad (2.2.10)$$

$$E_{ij+ab} - E_0 = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \quad (2.2.11)$$

Application of Rayleigh-Schrödinger perturbation theory¹⁸ leads to the correction terms directly. The first-order correction to the energy is

$$E^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle = V_{00} \quad (2.2.12)$$

The energy corrected to the first-order is, therefore

$$\begin{aligned} E^{(0)} + E^{(1)} &= \sum_i^N \epsilon_i + \langle \Psi_0 | V | \Psi_0 \rangle \\ &= \sum_i^N \epsilon_i - \frac{1}{2} \sum_i^N \sum_j^N (J_{ij} - K_{ij}) \end{aligned} \quad (2.2.13)$$

which is exactly the Hartree-Fock energy. Thus the Hartree-Fock energy is said to be correct to the first-order.

The second-order term, the leading term for the energy correction, has the form

$$E^{(2)} = \sum_s^D \frac{V_{0s} \cdot V_{s0}}{E_0 - E_s} \quad (2.2.14)$$

The sum over s is in the first place over all eigenfunctions of H_0 except Ψ_0 . However, as a consequence of Brillouin's theorem¹⁹ which states that the matrix element of the many-electron Hamiltonian H between the determinant Ψ_0 and the determinant Ψ_s vanishes if Ψ_s differs

from Ψ_0 by one spin orbital and the fact that H contains only one- and two-electron terms, the matrix element vanishes too if Ψ_s differs from Ψ_0 by more than two spin orbitals. Thus V_{0s} is non-zero only when Ψ_s is a double substitution.

The third- and fourth-order terms are

$$E^{(3)} = \sum_{s,t}^D \frac{V_{0s}(V_{st} - V_{00}\delta_{st})V_{t0}}{(E_0 - E_s)(E_0 - E_t)} \quad (2.2.15)$$

and

$$E^{(4)} = - \sum_{s,t}^D \frac{V_{0s}V_{s0}V_{0t}V_{t0}}{(E_0 - E_s)(E_0 - E_t)^2} \quad (2.2.16)$$

$$+ \sum_{s,u}^D \sum_t^{\text{SDTQ}} \frac{V_{0s}(V_{st} - V_{00}\delta_{st})(V_{tu} - V_{00}\delta_{tu})V_{u0}}{(E_0 - E_s)(E_0 - E_t)(E_0 - E_u)}$$

where δ_{xy} is called the Kronecker delta and is defined by

$$\delta_{xy} = \begin{cases} 1, & \text{if } x = y \\ 0, & \text{if } x \neq y \end{cases}$$

The third-order term involves only double substitutions, whereas, the fourth-order term has contributions from single, double, triple and quadruple substitutions. Higher substitutions do not contribute to the fourth-order energy because of the one- and two-electron character of the Hamiltonian.

The coefficients $a_s^{(i)}$ can also be obtained directly.¹⁸ The first-order wavefunction coefficients have the form

$$a_s^{(1)} = \frac{V_{s0}}{(E_0 - E_s)} \quad (2.2.17)$$

and because V_{s0} vanishes unless s is a double substitution, the first-order wavefunction correction is

$$\Psi^{(1)} = \sum_s^D a_s^{(1)} \Psi_s \quad (2.2.18)$$

The second-order wavefunction coefficients can be expressed as

$$a_s^{(2)} = - \frac{V_{00} V_{s0}}{(E_0 - E_s)^2} + \sum_t^D \frac{V_{t0} V_{st}}{(E_0 - E_s)(E_0 - E_t)} \quad (2.2.19)$$

$$\Psi^{(2)} = \sum_s^{SDTQ} a_s^{(2)} \Psi_s \quad (2.2.20)$$

Thus, single, triple and quadruple substitutions appear in the second-order wavefunction through their coupling with the doubles.

For any one-electron property P , the expectation value can be obtained from

$$\langle \Psi | P | \Psi \rangle \quad (2.2.21)$$

$$= \bar{N} \langle \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots | P | \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots \rangle$$

$$= \bar{N} [P^{(0)} + P^{(1)} + P^{(2)} + \dots]$$

where $\bar{N}$ is the normalization factor and $P^{(i)}$ is the i th-order correction

to the one-electron property

$$P^{(0)} = \langle \Psi_0 | P | \Psi_0 \rangle = P_{00} \quad (2.2.22)$$

$$P^{(1)} = 2 \langle \Psi_0 | P | \Psi^{(1)} \rangle = 0 \quad (2.2.23)$$

$$P^{(2)} = 2 \langle \Psi_0 | P | \Psi^{(2)} \rangle + \langle \Psi^{(1)} | P | \Psi^{(1)} \rangle \quad (2.2.24)$$

$$= 2 \sum_s^S a_s^{(2)} P_{0s} + \sum_{s,t}^D a_s^{(1)} a_t^{(1)} P_{st}$$

The matrix element P_{st} is defined as

$$P_{st} = \langle \Psi_s | P | \Psi_t \rangle \quad (2.2.25)$$

which is non-zero only when Ψ_s and Ψ_t differ by not more than one spin orbital. Since $P^{(1)}$ is zero, Hartree-Fock one-electron properties are correct to the first-order too. However, unlike energy, to have the one-electron properties corrected to the second-order, both single and double substitutions must be included.

Møller-Plesset perturbation theory is currently practical to the fourth-order.²⁰ It has the advantage of being size-consistent, that is the approximation scheme is equally good for molecules with different numbers of electrons. Nevertheless, like all other approximate methods, it has deficiencies, the most serious one is that the convergence is slow, i.e., in order to give an adequate approximation to the full configuration interaction result, many correction terms should be

included.²¹

2.3 Basis Sets

As mentioned in section 2.1, the use of basis sets is central to the quantum mechanics of molecular systems. Since the inclusion of complete basis sets is impractical, the choice of basis sets is critical for the accuracy of the calculations.

There are two main considerations in the choice of a basis function. The first is that one desires to use the most efficient and accurate functions possible, in the sense that the expansion

$$\chi = \sum_r c_r \phi_r \quad (2.1.27)$$

will require the fewest possible terms for an accurate representation of the molecular orbitals χ_i . The second consideration in the choice of a basis function is the speed of two-electron integral evaluation. Two types of functions, STOs (Slater-type-orbitals) and GTOs (Gaussian-type-orbitals) have assumed a dominant position in SCF calculations on molecules.²² Both sets of basis functions are usually centred on the nuclei. Slater-type functions (2.3.1), which were first

$$\phi_{nlm}(r, \theta, \varphi) = \bar{N}_n r^{n-1} e^{-\xi r} Y_{lm}(\theta, \varphi) \quad (2.3.1)$$

suggested by Slater,²³ provide a useful rough approximation to atomic SCF orbitals. However, the two-electron integrals involving Slater-type functions on several different centres are very difficult to evaluate.

Gaussian-type functions (2.3.2), which were proposed by Boys²⁴, have the

$$\phi_{kmn}(x,y,z) = \bar{N}_{kmn} x^k y^m z^n e^{-\xi r^2} \quad (2.3.2)$$

advantage that the multi-center, two-electron integrals can be easily evaluated. Gaussian-type functions have an inappropriate form however both in regions of space close to the nucleus upon which they are centered (they have no cusp) and in the long range region (they decay too rapidly). More Gaussian-type functions than Slater-type functions are required to approximate a given molecular orbital to a certain accuracy. By using a contracted Gaussian-type function, one can increase the efficiency of basis sets of Gaussian-type functions. A contracted Gaussian-type function is defined as a linear combination of Gaussian functions (primitives)^{17e,20,22,25}

$$\phi = \bar{N} \sum_i d_i g_i \quad (2.3.3)$$

where $\{g_i\}$ denotes a set of primitive functions of the same symmetry type and centred on the same nucleus, the d_i are a set of fixed contraction coefficients and $\bar{N}$ is a normalization constant. A contracted Gaussian-type function is a compromise between STOs and GTOs and are widely used in molecular calculations.

The choice of basis set is based on the consideration that the basis set should be flexible enough to provide "good" results over a wide range of molecular geometries and still small enough to leave the problem computationally tractable and economically within reason. There

are a vast number of basis sets in the literature. In the following paragraphs a few of the basis sets enjoying current widespread use and related to this thesis will be discussed.

Minimum basis sets (STO-nG),^{17e,20,22b,d,e} consist of one basis function, which is a linear combination of n primitive functions, for each SCF occupied atomic orbital. The main attraction of this basis set, other than its small size, is its effectiveness in predicting geometries and its interpretative value.

A minimum basis set has rather limited flexibility. The first step in improving upon the minimum basis set involves using two functions for each occupied SCF atomic orbital. The resulting basis set is called a double-zeta basis set. If two functions are used for valence orbitals only, the basis set is termed a split-valence basis set,^{17e,20,22d} for example, 4-31G and 6-31G. Addition of six cartesian d functions for heavy atoms gives the 6-31G* basis set. Further addition of a set of p functions to hydrogen results in the 6-31G** basis.^{17e,20,22d} The added higher angular momentum functions are called polarization functions as they describe the distortion of the atomic orbitals in the molecular environment. Polarization functions contribute significantly to calculated bond energies and are even more important for the treatment of electron correlation. Polarization functions are essential for an accurate description of the electronic structure of molecules.^{20,22b,d,e,26}

Augmenting the basis set with a set of diffuse s and p functions (which have small exponents, hence contribute significantly in the long range region) on heavy atoms gives the 6-31+G basis set and further

addition of a set of *s* functions on hydrogen atoms results in the 6-31++G basis set.^{20,22d} Since the radial extension of electrons in anions is greater than in neutral or positively charged molecules, the addition of diffuse functions is required for calculations on anions. Also, it is found that diffuse functions improve the description of lone pairs on first-row atoms as well.^{22d,e}

To improve upon the 6-31G* and 6-31G** basis sets, triple-zeta or quadruple-zeta basis sets are desirable. Also, more than one set of polarization functions and even higher angular momentum functions should be added.

Chapter 3

Transition State Structures of Model S_N2 Reactions

3.1 Overview

Transition state theory has achieved widespread acceptance as a tool for the interpretation of chemical reaction rates and has led to much insight into chemical and physical processes.^{27a,b} The fundamental assumptions involved in conventional transition state (TS) theory are that^{27c,d} molecules must traverse saddle points (transition states) of the potential energy surface and that the rate of reaction is proportional to the concentration of molecules in the TS, which in turn, is in "quasi-equilibrium" with the reactants. Thus, the position (in energy space) and structure (by structure I mean both geometrical and electronic) of the TS are key factors in interpreting the activation process and predicting reactivities.

The original concept of the TS structure is associated with the names of Polanyi, Evans and Bell.²⁸ The TS structure is believed to be a mixing of initial (reactants) and final (products) states. The electronic structure of the TS is characterized by^{28c,g}

$$\psi_{TS} = 2^{-1/2}(\psi_i + \psi_f) \quad (3.1.1)$$

where ψ_i is the initial state and ψ_f is the final state. The equal contribution of initial and final states to the TS is based on the assumption that the TS occurs in the vicinity of the intersection point

of initial and final states. The closely related Leffler-Hammond postulate states that the properties of the TS are intermediate between those of reactants and products.²⁹ For an exothermic reaction, the TS comes early and resembles the reactants more than the products while for an endothermic reaction, the TS comes late and resembles the products more than the reactants. Thornton³⁰ first realized that the topological character of the potential surface allows both parallel and perpendicular motion of the TS along the reaction coordinate. Parallel motion corresponds closely to predictions based on the Leffler-Hammond postulate. The TS resembles the one which has relatively high energy. However, the perpendicular motion enables the TS to take on characteristics which differ from those of the reactants and products and the TS resembles the one which has relatively low energy. Thornton pointed out that the previously neglected perpendicular motion is not small in all cases. Thus, the TS, in general, can not be completely described only by reactants and products.

Recently, Shaik and Pross proposed a valence-bond configuration mixing model³¹ (VBCM) to conceptualize TS structures, activation barriers and reactivities. According to this model, the reaction profile may be built up using a linear combination of valence-bond configurations and the TS can be approximated as a linear combination of valence-bond configurations as well. Thus, for simple S_N2 (for substitution, nucleophilic, bimolecular) reactions



where N^- is the entering nucleophile and X^- is the leaving group, the important configurations are:



and the TS wavefunction can be approximated as^{31d}

$$\psi_{TS} = a' [2^{-1/2}(\psi_1 + \psi_2)] + b'\psi_3 + c'\psi_4 \quad (3.1.3)$$

where

$$(a')^2 + (b')^2 + (c')^2 = 1 \text{ and } a' > b', c'$$

The form of the TS wavefunction assumes that the charges on N and X are equal and not related to the position of the TS along the reaction coordinate.^{31b}

Whereas transition states are not subject to experimental scrutiny, at least at present, the development of analytical procedures for the calculation of first and second derivatives of the energy and of methods for the location of minima and saddle points using this information have made theoretical studies of equilibrium geometries routine and studies of transition states tractable.³² A reliable charge partitioning scheme is available now due to the work of Bader and co-workers^{33a}. The corresponding post-Hartree-Fock analysis is made practical by Boyd and Wang.^{33b}

The purpose of this study is to provide ab initio results on S_N2

reactions with emphasis on the electronic structure of the TS. In this chapter, the TS structures of model S_N2 reactions (eq. 3.1.2) are reported. In all model reactions $R = CH_3$ and $N = H$ or F , where $X = H$, NH_2 , OH , F , NC, CCH, CN, SH and Cl; when $N = OH$, CN, SH and Cl, $X = H$, OH , F , CN, SH or Cl. In ambiguous cases the atom bonded directly to R is underlined. The computational details are given in the next section, while energies, geometries and topological properties are reported in section 3.3 followed by the charge and electronic structure analysis in section 3.4. In section 3.5, the results obtained by Mulliken population analysis are compared with the results obtained by integrating the electron density over the atomic basins. In the final section, 3.6, several computational methods are compared.

3.2 Computational Methods

The properties of interest in this study are geometries, one-electron distributions and associated properties, and the energetics of reactions (3.1.2). The basis sets and computational methods have been chosen so as to obtain, at least, qualitatively accurate results. Thus, the extended basis set 6-31G augmented with polarization functions was selected since previous research has shown that split-valence plus polarization basis sets yield similar trends for topological properties as the larger basis sets.³⁴ Also, diffuse functions were added to the basis sets to account for the long radial distributions of anionic systems. Diffuse functions and polarization functions were added to the basis sets of all atoms (standard notation 6-31++G**) except the three methyl hydrogen atoms for which the 6-31G basis set was used. This is justified by the fact that

omission of the polarization and diffuse functions on these atoms has only a small effect on the calculated results, while making the computation tractable.³⁵

The simple single-determinant HF method is believed³⁶ to give a qualitatively correct description of the potential surface of the reactions, and therefore the HF wavefunction is used as the zero-order wavefunction.

To account for the electron correlation effect, the post-Hartree-Fock method, second-order Møller-Plesset perturbation theory (MP2), was chosen, since it has the advantage of being size consistent, a very important property in the study of chemical reactivity.³⁷ At the MP2 level, two types of calculation were performed, namely, the single point calculations carried out at the geometries optimized by HF method (MP2/6-31++G**//HF/6-31++G**) and the optimized MP2 calculations (i.e. MP2/6-31++G**//MP2/6-31++G**). The purpose is to investigate the quality of the single point calculation especially on one-electron properities. Although single point calculations are frequently performed for the TS, detailed comparisons have not appeared in the literature.

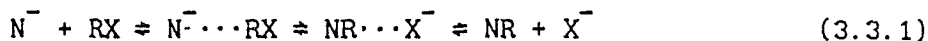
At the MP2 level, all single- and double-substitutions are included. Therefore, the energies and one-electron properties are both corrected to the second-order.

The HF and MP2 calculations were obtained by using the GAUSSIAN 80 and GAUSSIAN 86 computer programs.³⁸ Topological properties were calculated by using the PROAIM package^{33a} and a modified PROAIM package.^{33b} All calculations were performed on Perkin-Elmer 3230 and VAX 8800 computers.

All geometries were fully or partially optimized subject to C_{3v} , C_2 and C_s symmetry constraints as indicated. Only the back-side attack path³⁹ is considered in this thesis.

3.3 Transition State Properties

The experimental study of gas-phase S_N2 reactions became possible in the late 1960's with the development of a number of mass spectrometric techniques.⁴⁰ Studies of S_N2 reactions in the gas phase and in solution revealed two important differences.⁴¹ Firstly, gas-phase reactions are up to 20 orders of magnitude faster than their counterparts in solution, i.e., the gas-phase activation barriers are much lower. Secondly, the potential energy profile is of a double-well type in the gas phase (Fig. 3.3.1), but it has a unimodal shape in solution. The gas-phase reaction involves three steps,^{41a-c} (see eq.3.3.1.). The first step is the



formation of the reactant ion-molecule complex, the second step is the conversion of the reactant ion-molecule complex to the product ion-molecule complex, and the third and final step involves the relaxation of the product ion-molecule complex to yield the product. The energies shown in Fig. 3.3.1 are defined in eq. 3.3.2 to 3.3.7.

$$\Delta E_c(I) = E(N^- \cdots RX) - E(N^- + RX) \quad (3.3.2)$$

is the energy change upon the formation of the reactant ion-molecule

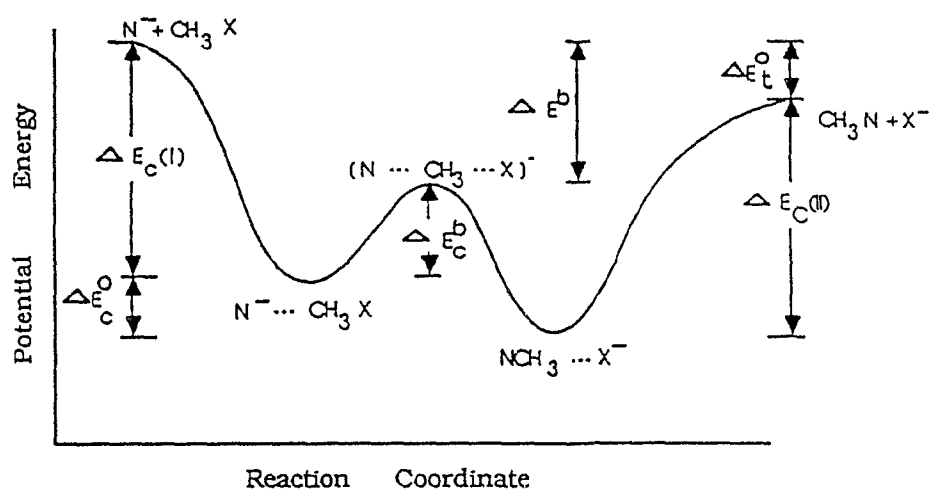


Figure 3.3.1 Schematic energy profile of a gas-phase S_N2 reaction.

complex from the reactant,

$$\Delta E_c(II) = E(NR \cdots X^-) - E(NR+X^-) \quad (3.3.3)$$

is the energy change upon the formation of the product ion-molecule complex from the product,

$$\Delta E_c^b = E([N \cdots R \cdots X]^-) - E(N^- \cdots RX) \quad (3.3.4)$$

is the energy barrier for the second step of the reaction,

$$\Delta E_c^\circ = E(NR \cdots X^-) - E(N^- \cdots RX) \quad (3.3.5)$$

is the energy change for the second step of the reaction,

$$\Delta E^b = E([N \cdots R \cdots X]^-) - E(N^-+RX) \quad (3.3.6)$$

is the energy barrier for the entire reaction and

$$\Delta E_t^\circ = E(NR+X^-) - E(N^-+RX) \quad (3.3.7)$$

is the energy change for the gas-phase reaction. Table 3.3.1 gives the HF results, while Tables 3.3.2 and 3.3.3 list the MP2 single point (MP2') and MP2 optimized results (MP2), respectively. Some available experimental results⁴² are listed in Table 3.3.4 together with the MP2' results.⁴³ A direct comparison of the experimental activation energies

Table 3.3.1 Energies^a calculated at the RHF level^b (kJ/mol).

$N^- + RX$	$\Delta E_c(I)$	$\Delta E_c(II)$	ΔE_c^b	ΔE_c°	ΔE^b	ΔE_t°
$H^- + RH$	-0.63	-0.63	264.12	0.00	263.49	0.00
$H^- + RNH_2$	-6.18	-2.92	210.76	-38.90	204.57	-42.16
$H^- + ROH$	-15.55	-5.35	149.50	-112.05	133.95	-122.26
$H^- + RF$	-31.43	-4.10	82.11	-194.73	50.67	-222.06
$H^- + RNC$	-45.02	-1.65	83.40	-282.88	38.38	-326.35
$H^- + RCCH$	-18.68	-1.39	194.88	-116.98	176.20	-134.27
$H^- + RCN$	-47.14	-1.26	142.51	-200.71	95.37	-246.59
$H^- + RSH$	-20.65	-1.51	68.35	-285.91	47.70	-305.05
$H^- + RCl$	-36.17	-1.25	16.41	-373.94	-19.76	-408.86
$F^- + RH$	-4.10	-31.43	276.84	194.73	272.74	222.06
$F^- + RNH_2$	-15.73	-50.51	210.39	145.11	194.67	179.90
$F^- + ROH$	-30.28	-55.50	145.84	74.58	115.56	99.81
$F^- + RF$	-53.74	-53.74	77.55	0.00	23.81	0.00
$F^- + RNC$	-70.91	-36.16	76.00	-69.43	5.09	-104.18
$F^- + RCCH$	-35.82	-36.66	191.88	86.95	156.06	87.79
$F^- + RCN$	-71.97	-32.52	143.07	14.92	71.10	-24.52
$F^- + RSH$	-37.52	-31.28	67.01	-76.75	29.49	-82.98
$F^- + RCl$	-60.73	-33.64	12.51	-159.70	-48.22	-186.80

Table 3.3.1 (continued)

$N^- + RX$	$\Delta E_c(I)$	$\Delta E_c(II)$	ΔE_c^b	ΔE_c°	ΔE^b	ΔE_t°
$HO^- + RH$	-5.35	-15.55	261.56	112.05	256.21	122.26
$HO^- + ROH$	-31.93	-31.93	135.61	0.00	103.69	0.00
$HO^- + RF$	-55.50	-30.28	71.25	-74.58	15.75	-99.81
$HO^- + RCN$	-76.70	-17.12	140.10	-64.75	63.41	-124.33
$HO^- + RSH$	-40.87	-16.71	64.15	-158.63	23.28	-182.79
$HO^- + RCl$	-63.46	-17.88	12.42	-241.01	-51.04	-286.60
$NC^- + RH$	-1.26	-47.14	343.22	200.71	341.96	246.59
$NC^- + ROH$	-17.12	-76.70	204.86	64.75	187.74	124.33
$NC^- + RF$	-32.52	-71.97	128.15	-14.92	95.63	24.52
$NC^- + RCN$	-45.87	-45.87	194.19	0.00	143.32	0.00
$NC^- + RSH$	-20.99	-47.36	117.38	-84.83	96.39	-58.46
$NC^- + RCl$	-35.16	-49.08	48.19	-176.19	13.03	-162.27
$HS^- + RH$	-1.51	-20.65	354.26	285.91	352.75	305.05
$HS^- + ROH$	-16.71	-40.87	222.78	158.63	206.07	182.79
$HS^- + RF$	-31.28	-37.52	143.76	76.75	112.48	82.98
$HS^- + RCN$	-47.36	-7.86	202.21	84.83	154.85	58.46
$HS^- + RSH$	-22.00	-22.00	120.25	0.00	98.24	0.00
$HS^- + RCl$	-34.71	-22.66	49.55	-91.77	14.85	-103.81

Table 3.3.1 (continued)

$N^- + RX$	$\Delta E_c(I)$	$\Delta E_c(II)$	ΔE_c^b	ΔE_c°	ΔE^b	ΔE_t°
$Cl^- + RH$	-1.25	-36.17	390.35	373.94	389.10	408.86
$Cl^- + ROH$	-17.88	-63.46	253.44	241.02	235.56	286.60
$Cl^- + RF$	-33.64	-60.73	172.21	159.70	138.58	186.80
$Cl^- + RCN$	-49.08	-35.16	224.38	176.19	175.30	162.27
$Cl^- + RSH$	-22.66	-34.71	141.32	91.77	118.66	103.81
$Cl^- + RCl$	-37.15	-37.15	64.72	0.00	27.57	0.00

^a Energies are defined in Fig. 3.3.1 and the accompanying text.

^b The energy of methane was first calculated at HF/6-31+G**//HF/6-31+G* and HF/6-31++G**//HF/6-31+G* levels and then these values were used to extrapolate the energy corresponding to a basis set which has diffuse and polarization functions added to carbon and one of the hydrogen atoms. In doing so, the basis set is consistent with those used in ion-molecule complex and transition state calculations.

Table 3.3.2 Energies calculated at the MP2' level^a (kJ/mol).

$N^- + RX$	$\Delta E_c(I)$	$\Delta E_c(II)$	ΔE_c^b	ΔE_c°	ΔE^b	ΔE_t°
$H^- + RH$	-1.53	-1.53	235.15	0.00	233.62	0.00
$H^- + RNH_2$	-10.03	-6.07	150.45	-87.92	140.42	-91.88
$H^- + ROH$	-20.62	-9.23	87.14	-176.57	66.52	-187.97
$H^- + RF$	-36.71	-7.00	32.93	-257.47	-3.78	-287.18
$H^- + RNC$	-55.74	-3.92	60.83	-308.41	5.09	-360.23
$H^- + RCCH$	-23.93	-3.30	172.35	-127.13	148.42	-147.77
$H^- + RCN$	-51.49	-2.97	127.25	-206.61	75.76	-255.13
$H^- + RSH$	-24.92	-4.12	56.50	-275.74	31.58	-296.54
$H^- + RCl$	-38.53	-3.47	15.35	-364.49	-23.18	-399.55
$F^- + RH$	-7.00	-36.71	290.40	257.47	283.40	287.18
$F^- + RNH_2$	-20.92	-57.64	188.95	158.58	168.03	195.30
$F^- + ROH$	-35.76	-60.89	115.85	74.09	80.08	99.21
$F^- + RF$	-58.24	-58.24	52.70	0.00	-5.54	0.00
$F^- + RNC$	-80.23	-40.16	76.26	-32.97	-3.98	-73.05
$F^- + RCN$	-73.19	-37.32	153.94	67.92	80.75	32.05
$F^- + RSH$	-40.34	-38.68	79.79	-7.70	39.45	-9.36
$F^- + RCl$	-57.97	-39.31	25.13	-93.71	-32.84	-112.37
$HO^- + RH$	-9.23	-20.62	263.72	176.57	254.49	187.97
$HO^- + ROH$	-38.59	-38.59	98.49	0.00	59.90	0.00
$HO^- + RF$	-60.89	-35.76	41.76	-74.09	-19.13	-99.21
$HO^- + RCN$	-79.78	-21.80	145.76	-9.19	65.98	-67.16
$HO^- + RSH$	-45.07	-22.60	69.84	-86.11	24.77	-108.57

Table 3.3.2 (continued)

$N^- + RX$	$\Delta E_c(I)$	$\Delta E_c(II)$	ΔE_c^b	ΔE_c°	ΔE^b	ΔE_t°
$HO^- + RCl$	-61.39	-23.81	20.20	-174.00	-41.19	-211.59
$NC^- + RH$	-2.97	-51.48	333.86	206.61	330.89	255.13
$NC^- + ROH$	-21.80	-79.78	154.95	9.19	133.15	67.16
$NC^- + RF$	-37.32	-73.19	86.02	-67.92	48.70	-32.05
$NC^- + RCN$	-48.50	-48.50	191.02	0.00	142.52	0.00
$NC^- + RSH$	-24.76	-53.82	117.25	-70.47	32.49	-41.41
$NC^- + RCl$	-36.59	-54.24	56.94	-162.08	20.35	-144.42
$HS^- + RH$	-4.12	-24.92	332.24	275.74	328.12	296.54
$HS^- + ROH$	-22.60	-45.07	155.94	86.11	133.34	108.57
$HS^- + RF$	-38.68	-40.34	87.49	7.70	48.81	9.36
$HS^- + RCN$	-53.82	-24.76	187.72	70.47	133.90	41.41
$HS^- + RSH$	-27.59	-27.59	110.83	0.00	83.24	0.00
$HS^- + RCl$	-40.10	-27.43	52.61	-90.34	12.51	-103.02
$Cl^- + RH$	-3.47	-38.53	379.84	364.49	376.37	399.55
$Cl^- + ROH$	-23.81	-61.39	194.20	174.00	170.39	211.59
$Cl^- + RF$	-39.31	-57.97	118.84	93.71	79.53	112.37
$Cl^- + RCN$	-54.24	-36.59	219.02	162.08	164.78	144.42
$Cl^- + RSH$	-27.43	-40.10	142.95	90.34	115.53	103.02
$Cl^- + RCl$	-39.72	-39.72	75.44	0.00	35.72	0.00

^aThe energy of methane was calculated at MP2/6-31+G**//HF/6-31+G* and MP2/6-31++G**//HF/6-31+G* levels and then the energy corresponding to a basis with polarization and diffuse functions added to carbon and one of the hydrogen atoms was extrapolated.

Table 3.3.3 Energies calculated at the MP2 level^a (kJ/mol).

$N^- + RX$	$\Delta E_c(I)$	$\Delta E_c(II)$	ΔE_c^b	ΔE_c°	ΔE^b	ΔE_t°
$H^- + RH$	-2.07	-2.07	230.86	0.0	228.78	0.00
$H^- + RNH_2$	-10.95	-6.88	149.48	-87.37	138.53	-91.44
$H^- + ROH$	-21.39	-9.90	88.59	-174.83	67.20	-186.42
$H^- + RF$	-37.42	-7.17	37.36	-254.61	-0.06	-284.86
$H^- + RNC$	-57.30	-4.32	59.48	-308.37	2.19	-361.34
$H^- + RCCH$	-24.23	-3.66	170.69	-125.32	146.46	-145.90
$H^- + RCN$	-51.42	-3.35	126.23	-203.48	74.81	-251.55
$H^- + RSH$	-25.63	-5.61	53.65	-276.04	28.02	-296.06
$H^- + RCl$	-39.31	-4.01	13.11	-363.79	-26.20	-399.08
$F^- + RH$	-7.17	-37.42	291.98	254.61	284.80	284.86
$F^- + ROH$	-35.96	-61.40	116.13	73.00	80.17	98.44
$F^- + RF$	-58.21	-58.21	54.09	0.00	-4.12	0.00
$F^- + RCl$	-58.83	-39.92	25.56	-95.31	-33.27	-114.22
$Cl^- + RCl$	-40.42	-40.42	72.54	0.00	32.12	0.00

^a The energy of methane was calculated at MP2/6-31+G**//MP2/6-31+G* and MP2/6-31++G**//MP2/6-31+G* levels and then the energy corresponding to a basis set with polarization and diffuse functions added to the carbon and one of the hydrogen atoms was extrapolated.

Table 3.3.4 Experimental activation energies and heats of reactions
(kJ/mol).

$N^- + RX$	E_a	$-\Delta H$	MP2'	
			ΔE^b	$-\Delta E_t^\circ$
$H^- + RF$	16 ± 0.4	230 ± 30	-3.8	287
$HO^- + RF$	11 ± 0.8	75 ± 40	-19.1	99
$NC^- + RF$	≥ 16	20 ± 46	48.7	32
$H_2N^- + RF$	12 ± 0.4	130 ± 40	-27.3	195
$H^- + RCl$	2.6 ± 3.1	370 ± 40	-23.2	400
$F^- + RCl$	0.4 ± 0.4	130 ± 46	-32.8	112
$HO^- + RCl$	1.2 ± 0.60	210 ± 42	-41.1	212
$NC^- + RCl$	≥ 20	150 ± 50	20.4	144
$HS^- + RCl$	12 ± 0.4	92 ± 40	12.5	103

with potential barrier heights is not possible, in general, without taking into account the zero-point energy, rotational, translational, $\Delta(PV)$ and RT corrections. Furthermore, the E_a values were obtained by a different model for the rate constant calculations.^{41f} For a reaction with $N=H$, $X=F$, a recent study indicates that a ΔE^b value of about 4.2 kJ/mol would give a rate constant which agrees closely with the experimental results.⁸⁴ This work produced a $\Delta E^b = -3.8$ and -0.06 kJ/mol at the MP2' and MP2 levels, respectively.

Brauman *et al.*⁴⁴ have assumed that the well depth ($\Delta E_c(I)$ or $\Delta E_c(II)$) for the same X should be almost equal, as it mainly depends on the polarizability and dipole moment of the neutral molecule and not on the structure of the ion. The data in Tables 3.3.1-3.3.3 indicate that when $X = H$ (or when $N = H$), $\Delta E_c(I)$ (or $\Delta E_c(II)$) has its smallest absolute values. This can be understood by noting that RH does not have a permanent dipole moment, whereas when $X = \underline{C}N$ and $\underline{N}C$, RX has a large permanent dipole moment (see Table 3.3.5). Thus, $\Delta E_c(I)$ values are large when RX has a large dipole moment. Also, for the hard nucleophiles OH and F , the $\Delta E_c(I)$ values are usually large. Since the difference between ΔE^b and ΔE_c^b is equal to $\Delta E_c(I)$, the plot of ΔE^b vs. ΔE_c^b shows a good correlation except in the cases where $\underline{C}N$ is involved (see Fig. 3.3.2). A similar observation holds for the plot of ΔE_t° vs ΔE_c° (Fig. 3.3.3). For gas-phase S_N2 reactions, the second step is the critical step which is responsible for the wide variation in efficiencies.^{41c}

Nucleophilicity is defined as a kinetic property of a nucleophile and is measured by its rate constant for an S_N2 reaction.⁴⁶ The value of ΔE^b or ΔE_c^b serves as an index of the nucleophilicity. The data in Tables

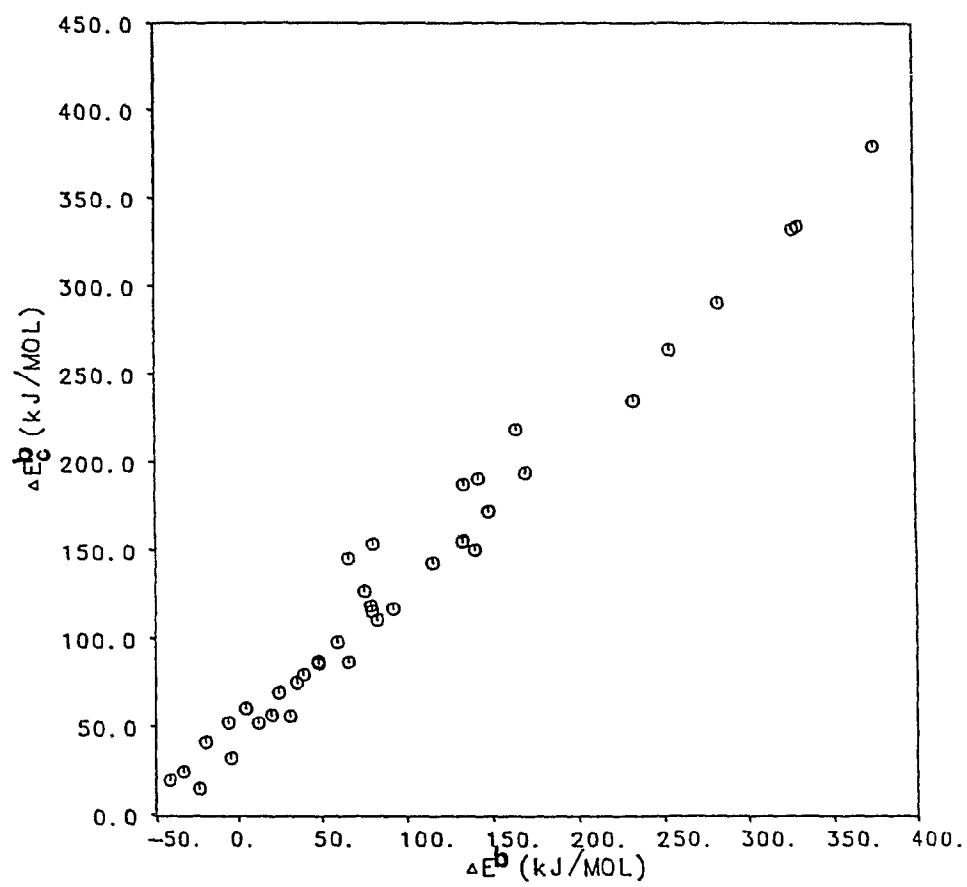


Figure 3.3.2 Comparison of ΔE^b with ΔE_C^b at the MP2' level.

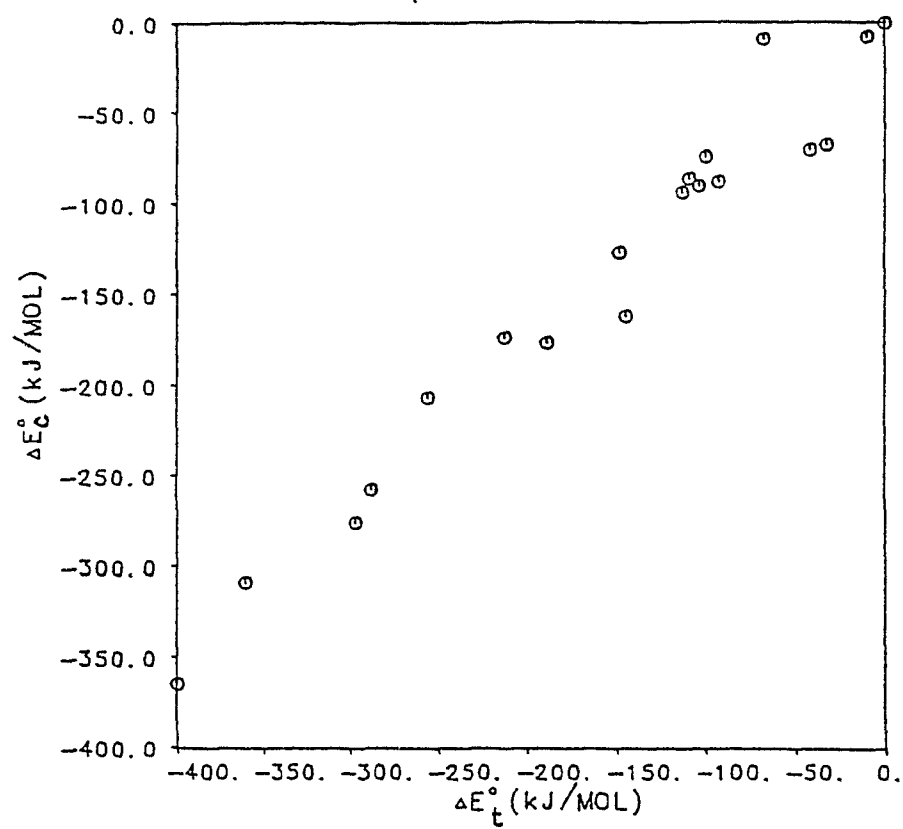


Figure 3.3.3 Comparison of ΔE_t° with ΔE_C° at the MP2' level.

Table 3.3.5 Electronic dipole moments of RX molecules (D).

RX	Method			Expt. ^a
	RHF	MP2'	MP2	
RH	0.00	0.00	0.00	0.00
RNH ₂	1.50	1.49	1.52	1.238
ROH	1.97	1.85	1.91	1.70 ^b
RF	2.19	1.83	1.95	1.857
RNC	3.70	4.88	4.90	3.83
RCCH	0.75	0.92	0.94	0.75
RCN	4.20	3.95	3.94	3.913
RSN	1.83	1.76	1.74	1.52 ^b
RCI	2.31	2.02	1.99	1.869

^a Experimental data from reference 45.

^b Data from reference 20 and references therein.

3.3.1-3.3.3 show that the nucleophilicity order is usually $\text{H}^- > \text{OH}^- > \text{F}^- > \text{SH}^- \sim \text{CN}^- > \text{Cl}^-$ and the leaving group follows the order $\text{Cl}^- > \text{F}^- > \text{NC}^- > \text{SH}^- > \text{OH}^- > \text{CN}^- > \text{NH}_2^- > \text{CCH}^- > \text{H}^-$. The theoretical results are consistent with the experimental results.^{41a,42}

Table 3.3.6 lists optimized bond lengths between C and N ($R_{\text{C-N}}$) and C and X ($R_{\text{C-X}}$) in the TS. The detailed geometry structures can be found in the appendix.

Table 3.3.7 gives critical point data in the TS, where $r_{\text{C-N}}$ is the distance between N and C-N bond critical point and $\rho_{\text{C-N}}$ is the electron density at C-N bond critical point. The results demonstrate that the electron density at the bond critical point is related to the bond length. For a series of reactions with the same N and different X, as the bond length increases, the distance between N and the bond critical point increases and the electron density decreases.

3.4 Electronic Structures of the Transition States

According to the valence-bond configuration mixing model, the TS wavefunction can be approximated as a linear combination of the important valence bond (VB) configurations. Shaik and Pross proposed that for simple $\text{S}_{\text{N}}2$ reactions, the TS wavefunction can be written as in eq. 3.1.3, i.e. valence bond configurations 1 and 2 make equal contributions to the TS. Based on this assumption, they further stated that the charges on nucleophile N and leaving group X are equal in the TS and not related to the position of the TS along the reaction coordinate.^{31b}

The concept of charge transfer is central to organic chemistry in

Table 3.3.6 RHF and MP2 bond lengths in the transition state (Å).

$[\text{N}\cdots\text{R}\cdots\text{X}]^-$	$\text{R}_{\text{C-N}}$		$\text{R}_{\text{C-X}}$	
	RHF	MP2	RHF	MP2
$[\text{H}\cdots\text{R}\cdots\text{H}]^-$	1.690	1.589	1.690	1.589
$[\text{H}\cdots\text{R}\cdots\text{NH}_2]^-$	1.738	1.712	2.029	1.962
$[\text{H}\cdots\text{R}\cdots\text{OH}]^-$	1.791	1.803	1.890	1.821
$[\text{H}\cdots\text{R}\cdots\text{F}]^-$	1.874	1.928	1.764	1.696
$[\text{H}\cdots\text{R}\cdots\text{NC}]^-$	2.004	1.964	1.851	1.774
$[\text{H}\cdots\text{R}\cdots\text{CCH}]^-$	1.846	1.780	2.057	1.982
$[\text{H}\cdots\text{R}\cdots\text{CN}]^-$	1.909	1.845	1.996	1.927
$[\text{H}\cdots\text{R}\cdots\text{SH}]^-$	2.029	1.952	2.253	2.183
$[\text{H}\cdots\text{R}\cdots\text{Cl}]^-$	2.235	2.152	2.086	2.027
$[\text{F}\cdots\text{R}\cdots\text{NH}_2]^-$	1.761	1.710	2.144	2.178
$[\text{F}\cdots\text{R}\cdots\text{OH}]^-$	1.795	1.760	1.990	2.008
$[\text{F}\cdots\text{R}\cdots\text{F}]^-$	1.846	1.836	1.846	1.836
$[\text{F}\cdots\text{R}\cdots\text{NC}]^-$	1.950		1.903	
$[\text{F}\cdots\text{R}\cdots\text{CCH}]^-$	1.840		2.143	
$[\text{F}\cdots\text{R}\cdots\text{CN}]^-$	1.882	1.829	2.072	2.065
$[\text{F}\cdots\text{R}\cdots\text{SH}]^-$	1.977	1.887	2.331	2.328
$[\text{F}\cdots\text{R}\cdots\text{Cl}]^-$	2.126	2.013	2.133	2.142
$[\text{HO}\cdots\text{R}\cdots\text{OH}]^-$	1.931		1.931	
$[\text{HO}\cdots\text{R}\cdots\text{CN}]^-$	2.013		2.026	
$[\text{HO}\cdots\text{R}\cdots\text{SH}]^-$	2.119		2.287	
$[\text{HO}\cdots\text{R}\cdots\text{Cl}]^-$	2.267		2.103	

Table 3.3.6 (continued)

$[N \cdots R \cdots X]^-$	R_{C-N}		R_{C-X}	
	RHF	MP2	RHF	MP2
$[NC \cdots R \cdots CN]^-$	2.136		2.136	
$[NC \cdots R \cdots SH]^-$	2.198		2.418	
$[NC \cdots R \cdots Cl]^-$	2.318		2.247	
$[HS \cdots R \cdots SH]^-$	2.474		2.474	
$[HS \cdots R \cdots Cl]^-$	2.602		2.282	
$[Cl \cdots R \cdots Cl]^-$	2.393	2.316	2.393	2.316

Table 3.3.7 Critical points of transition state structures at the RHF,
MP2' and MP2 levels (a.u.).

$[N \cdots R \cdots X]^-$	r_{C-N}			ρ_{C-N}		
	RHF	MP2'	MP2	RHF	MP2'	MP2
$[H \cdots R \cdots H]^-$	1.351	1.286	1.189	0.068	0.071	0.086
$[H \cdots R \cdots NH_2]^-$	1.440	1.363	1.340	0.061	0.064	0.066
$[H \cdots R \cdots OH]^-$	1.512	1.456	1.446	0.058	0.058	0.054
$[H \cdots R \cdots F]^-$	1.608	1.533	1.592	0.045	0.048	0.042
$[H \cdots R \cdots \underline{NC}]^-$	1.739	2.114	1.633	0.035	0.038	0.039
$[H \cdots R \cdots CCH]^-$	1.556	1.484	1.420	0.049	0.052	0.058
$[H \cdots R \cdots \underline{CN}]^-$	1.622	1.554	1.491	0.043	0.046	0.050
$[H \cdots R \cdots SH]^-$	1.712	1.646	1.567	0.035	0.036	0.041
$[H \cdots R \cdots Cl]^-$	1.941	1.883	1.793	0.023	0.024	0.027
$[F \cdots R \cdots H]^-$	1.945	1.853	1.818	0.090	0.105	0.123
$[F \cdots R \cdots NH_2]^-$	1.962	1.874	1.844	0.089	0.103	0.117
$[F \cdots R \cdots OH]^-$	1.986	1.903	1.879	0.081	0.095	0.103
$[F \cdots R \cdots F]^-$	2.019	1.943	1.937	0.071	0.084	0.086
$[F \cdots R \cdots \underline{NC}]^-$	2.079	2.023		0.057	0.066	
$[F \cdots R \cdots CCH]^-$	2.002			0.074		
$[F \cdots R \cdots \underline{CN}]^-$	2.026	1.961	1.924	0.068	0.079	0.089
$[F \cdots R \cdots SH]^-$	2.080	2.015	1.948	0.056	0.065	0.079
$[F \cdots R \cdots Cl]^-$	2.191	2.143	2.052	0.040	0.046	0.059
$[HO \cdots R \cdots H]^-$	2.044	1.955	1.905	0.081	0.089	0.106
$[HO \cdots R \cdots OH]^-$	2.099	2.016		0.071	0.079	
$[HO \cdots R \cdots F]^-$	2.146	2.069	2.080	0.061	0.068	0.066

Table 3.3.7 (continued)

$[\text{N}\cdots\text{R}\cdots\text{X}]^-$	$r_{\text{C-N}}$			$\rho_{\text{C-N}}$		
	RHF	MP2'	MP2	RHF	MP2'	MP2
$[\text{HO}\cdots\text{R}\cdots\text{CN}]^-$	2.146	2.077		0.059	0.066	
$[\text{HO}\cdots\text{R}\cdots\text{SH}]^-$	2.214	2.142		0.048	0.053	
$[\text{HO}\cdots\text{R}\cdots\text{Cl}]^-$	2.327	2.273		0.034	0.038	
$[\text{NC}\cdots\text{R}\cdots\text{H}]^-$	2.166	2.076	2.010	0.079	0.083	0.095
$[\text{NC}\cdots\text{R}\cdots\text{OH}]^-$	2.230	2.144		0.072	0.076	
$[\text{NC}\cdots\text{R}\cdots\text{F}]^-$	2.279	2.196	2.186	0.064	0.068	0.068
$[\text{NC}\cdots\text{R}\cdots\text{CN}]^-$	2.319	2.244		0.057	0.060	
$[\text{NC}\cdots\text{R}\cdots\text{SH}]^-$	2.360	2.279		0.051	0.054	
$[\text{NC}\cdots\text{R}\cdots\text{Cl}]^-$	2.481	2.408		0.039	0.041	
$[\text{HS}\cdots\text{R}\cdots\text{H}]^-$	2.463	2.366	2.288	0.071	0.073	0.084
$[\text{HS}\cdots\text{R}\cdots\text{OH}]^-$	2.546	2.444		0.064	0.068	
$[\text{HS}\cdots\text{R}\cdots\text{F}]^-$	2.605	2.502	2.506	0.058	0.062	0.061
$[\text{HS}\cdots\text{R}\cdots\text{CN}]^-$	2.680	2.586		0.050	0.053	
$[\text{HS}\cdots\text{R}\cdots\text{SH}]^-$	2.716	2.619		0.045	0.048	
$[\text{HS}\cdots\text{R}\cdots\text{Cl}]^-$	2.866	2.778		0.034	0.037	
$[\text{Cl}\cdots\text{R}\cdots\text{H}]^-$	2.343	2.243	2.183	0.086	0.092	0.105
$[\text{Cl}\cdots\text{R}\cdots\text{OH}]^-$	2.393	2.294		0.081	0.087	
$[\text{Cl}\cdots\text{R}\cdots\text{F}]^-$	2.428	2.329	2.339	0.075	0.081	0.079
$[\text{Cl}\cdots\text{R}\cdots\text{CN}]^-$	2.521	2.433		0.059	0.064	
$[\text{Cl}\cdots\text{R}\cdots\text{SH}]^-$	2.540	2.445		0.055	0.060	
$[\text{Cl}\cdots\text{R}\cdots\text{Cl}]^-$	2.657	2.571	2.494	0.043	0.047	0.055

that most reactions involve electron transfer in the transition state to some extent. In this section, the charges obtained by integration of the electron density over atomic basins (eq. 1.2.8) are reported and the configuration analysis is followed. Also the question of whether or not the charge development is related to the position of the TS is discussed.

To understand the charge distribution in the TS, it is helpful to study the charge distribution in the reactants and products. For this purpose, the integrated charges on X in molecules RX ($R = CH_3$) are provided in Table 3.4.1. The MP2 charges on X vary from +0.069 to -0.651. This large variation in charge transfer is a direct result of the different electronegativities of the X groups.

Integrated charges on nucleophile N (Q_N) and leaving group X (Q_X) in the TS are tabulated in Table 3.4.2. There are several immediate observations. First of all, at all three computational levels, the charges on N or X differ from reaction to reaction. Secondly, at the RHF level, the charges on N are not equal to the charges on X unless $N = X$, i.e., in a symmetric reaction. This is also observed at the MP2' level. However, at the highest level, MP2, there are certain cases where $Q_N \approx Q_X$.

Using the integrated charges, it is possible to estimate the upper bounds of the contributions of various configuration to the TS.

For simple S_N2 reactions, the important valence-bond configurations are:^{31d}

Table 3.4.1 Integrated charges on X in CH_3X at the RHF, MP2' and MP2 levels (e).

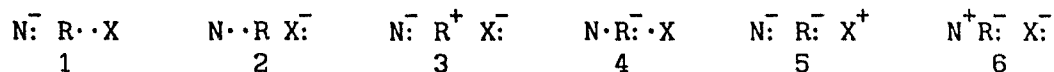
RX	$-Q_X$		
	RHF	MP2'	MP2
RH	0.007	-0.066	-0.069
RNH_2	0.465	0.350	0.337
ROH	0.652	0.545	0.508
RF	0.741	0.626	0.600
RNC	0.708	0.650	0.651
RCCH	0.293	0.290	0.247
RCN	0.391	0.328	0.325
RSH	0.048	-0.003	-0.008
RCI	0.323	0.224	0.219

Table 3.4.2 Transition state integrated charges obtained at the RHF,
MP2' and MP2 levels (e).

$[N \cdots R \cdots X]^-$	RHF		MP2'		MP2	
	$-Q_N$	$-Q_X$	$-Q_N$	$-Q_X$	$-Q_N$	$-Q_X$
$[H \cdots R \cdots H]^-$	0.601	0.601	0.520	0.520	0.516	0.516
$[H \cdots R \cdots NH_2]^-$	0.648	0.720	0.554	0.640	0.597	0.603
$[H \cdots R \cdots OH]^-$	0.674	0.779	0.586	0.677	0.643	0.635
$[H \cdots R \cdots F]^-$	0.711	0.832	0.629	0.717	0.700	0.679
$[H \cdots R \cdots \underline{NC}]^-$	0.750	0.792	0.657	0.724	0.698	0.705
$[H \cdots R \cdots CCH]^-$	0.687	0.722	0.582	0.665	0.598	0.655
$[H \cdots R \cdots \underline{CN}]^-$	0.705	0.734	0.601	0.667	0.617	0.683
$[H \cdots R \cdots SH]^-$	0.727	0.607	0.626	0.519	0.637	0.488
$[H \cdots R \cdots Cl]^-$	0.799	0.636	0.719	0.535	0.725	0.513
$[F \cdots R \cdots NH_2]^-$	0.835	0.795	0.727	0.718	0.700	0.750
$[F \cdots R \cdots OH]^-$	0.845	0.827	0.740	0.738	0.723	0.749
$[F \cdots R \cdots F]^-$	0.862	0.862	0.764	0.764	0.762	0.762
$[F \cdots R \cdots \underline{NC}]^-$	0.890	0.821	0.771	0.788		
$[F \cdots R \cdots CCH]^-$	0.857	0.779				
$[F \cdots R \cdots \underline{CN}]^-$	0.868	0.779	0.765	0.721	0.746	0.746
$[F \cdots R \cdots SH]^-$	0.889	0.679	0.791	0.584	0.757	0.628
$[F \cdots R \cdots Cl]^-$	0.926	0.681	0.849	0.585	0.814	0.625
$[HO \cdots R \cdots OH]^-$	0.803	0.803	0.708	0.708		
$[HO \cdots R \cdots \underline{CN}]^-$	0.830	0.753	0.732	0.703		
$[HO \cdots R \cdots SH]^-$	0.855	0.651	0.759	0.553		

Table 3.4.2 (continued)

$[N \cdots R \cdots X]^-$	RHF		MP2'		MP2	
	$-Q_N$	$-Q_X$	$-Q_N$	$-Q_X$	$-Q_N$	$-Q_X$
$[HO \cdots R \cdots Cl]^-$	0.897	0.661	0.819	0.564		
$[NC \cdots R \cdots CN]^-$	0.794	0.794	0.722	0.722		
$[NC \cdots R \cdots SH]^-$	0.794	0.709	0.738	0.600		
$[NC \cdots R \cdots Cl]^-$	0.851	0.730	0.804	0.607		
$[HS \cdots R \cdots SH]^-$	0.719	0.719	0.618	0.618		
$[HS \cdots R \cdots Cl]^-$	0.782	0.740	0.682	0.641		
$[Cl \cdots R \cdots Cl]^-$	0.794	0.794	0.703	0.703	0.695	0.695



Thus, the TS wavefunction can be written as a linear combination as follows:

$$\Psi_{\text{TS}} = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 + c_5\psi_5 + c_6\psi_6 \quad (3.4.1)$$

The reactant wavefunction (Ψ_r) can be written as a linear combination of VB configurations which contain a negative charge on N⁴⁷

$$\Psi_r = a_1\psi_1 + a_2\psi_3 + a_3\psi_5 \quad (3.4.2)$$

and the product (Ψ_p) can be written as an equivalent linear combination of VB configurations involving a negative charge on X⁴⁷

$$\Psi_p = b_1\psi_2 + b_2\psi_3 + b_3\psi_6 \quad (3.4.3)$$

The contributions of ψ_5 and ψ_r to Ψ_{TS} are small and relatively unimportant since they involve a two-electron transfer to form high-energy configurations.^{31d} Hence

$$\Psi_{\text{TS}} \approx c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 \quad (3.4.4)$$

or using reactant and product wavefunction

$$\Psi_{TS} \approx a\Psi_r + b\Psi_p + c\psi_3 + d\psi_4 \quad (3.4.5)$$

According to the molecular structure theory,¹ the charge on atom A in the TS is defined as

$$Q_A = Z_A - \int_A \rho_{TS}(r) dr \quad (3.4.6)$$

Substituting eq. 3.4.5 into eq. 3.4.6 and assuming that cross terms are zero leads to the relationship between the charge on atom A in the TS and the charges on atom A in various configurations

$$Q_A = a^2 Q_A(\Psi_r) + b^2 Q_A(\Psi_p) + c^2 Q_A(\psi_3) + d^2 Q_A(\psi_4) \quad (3.4.7)$$

where $Q_A(\psi_x) = Z_A - \int_A \rho_x(r) dr$.

This leads to a set of linear independent equations

$$\left\{ \begin{array}{l} Q_X = a^2 Q_X(\Psi_r) + b^2 Q_X(\Psi_p) + c^2 Q_X(\psi_3) + d^2 Q_X(\psi_4) \\ Q_N = a^2 Q_N(\Psi_r) + b^2 Q_N(\Psi_p) + c^2 Q_N(\psi_3) + d^2 Q_N(\psi_4) \\ a^2 + b^2 + c^2 + d^2 = 1 \end{array} \right. \quad (3.4.8)$$

The charges Q_A , $Q_A(\Psi_r)$ and $Q_A(\Psi_p)$ can be obtained by integrating the corresponding wavefunction over the atomic basin of A. The results are shown in Tables 3.4.1-3.4.2. The charges $Q_A(\psi_3)$, $Q_A(\psi_4)$, etc., can be obtained directly from the VB configurations. They are

$$\begin{array}{ll}
 Q_X(\psi_1) = 0, & Q_N(\psi_1) = -1 \\
 Q_X(\psi_2) = -1, & Q_N(\psi_2) = 0 \\
 Q_X(\psi_3) = -1, & Q_N(\psi_3) = -1 \\
 Q_X(\psi_4) = 0, & Q_N(\psi_4) = 0
 \end{array}$$

By setting c^2 or $d^2 = 0$, it is possible to evaluate a^2 , b^2 , d^2 or c^2 . In each case, the choice between $c^2 = 0$ or $d^2 = 0$ is made on the basis that only one of these two possibilities yields reasonable results, i.e., the coefficients are real numbers. For example, if c^2 is set equal to zero for $N = X = H$, then $a^2 = b^2 = 0.50$ at the RHF level. In which case d^2 is a complex number. Consequently, the solution given in Table 3.4.3 ($a^2 = b^2 = 0.40$ and $c^2 = 0.20$, $d^2 = 0$) is chosen. The results obtained at the MP2' and MP2 levels are given in Table 3.4.4 and 3.4.5, respectively.

At all three calculation levels, the reactant contributions to the transition state (a^2) are not equal to the product contributions (b^2). In some of the reactions, there is considerable contribution from VB configuration ψ_3 to the TS ($c^2 > 0.1$ at the MP2' level⁴⁸). Thus, using Thornton's parallel and perpendicular concept, these reactions involve considerable perpendicular motion of the TS along the reaction coordinate. Furthermore, it appears that these reactions usually consist of N and X which have small electronegativities, for example H, CCH, CN, SH and Cl (the data in Table 3.4.1 provide information on the electronegativity of X in RX, since a electronegative X has a large negative charge). Thus, the reaction can be classified according to the contribution of ψ_3 to the transition state. With the same nucleophile and within each type of reaction, the ratio of the product contribution

Table 3.4.3 Configuration analysis at the RHF level.

$[N\cdots R\cdots X]^-$	a^2	b^2	c^2	d^2	$-\frac{b^2}{a^2}$
$[H\cdots R\cdots H]^-$	0.40	0.40	0.20	0.00	1.00
$[H\cdots R\cdots NH_2]^-$	0.52	0.35	0.12	0.00	0.68
$[H\cdots R\cdots OH]^-$	0.63	0.33	0.04	0.00	0.52
$[H\cdots R\cdots F]^-$	0.66	0.29	0.05	0.00	0.45
$[H\cdots R\cdots \underline{NC}]^-$	0.71	0.25	0.04	0.00	0.35
$[H\cdots R\cdots CCH]^-$	0.39	0.32	0.29	0.00	0.80
$[H\cdots R\cdots \underline{CN}]^-$	0.44	0.30	0.27	0.00	0.68
$[H\cdots R\cdots SH]^-$	0.41	0.28	0.31	0.00	0.67
$[H\cdots R\cdots Cl]^-$	0.53	0.20	0.27	0.00	0.38
$[F\cdots R\cdots H]^-$	0.29	0.66	0.05	0.00	2.23
$[F\cdots R\cdots NH_2]^-$	0.37	0.62	0.00	0.00	1.66
$[F\cdots R\cdots OH]^-$	0.45	0.53	0.00	0.02	1.19
$[F\cdots R\cdots F]^-$	0.49	0.49	0.00	0.01	1.00
$[F\cdots R\cdots \underline{NC}]^-$	0.59	0.40	0.00	0.01	0.68
$[F\cdots R\cdots CCH]^-$	0.31	0.55	0.13	0.00	1.76
$[F\cdots R\cdots \underline{CN}]^-$	0.36	0.51	0.13	0.00	1.40
$[F\cdots R\cdots SH]^-$	0.32	0.43	0.25	0.00	1.32
$[F\cdots R\cdots Cl]^-$	0.47	0.29	0.24	0.00	0.61
$[HO\cdots R\cdots H]^-$	0.33	0.63	0.04	0.00	1.94
$[HO\cdots R\cdots OH]^-$	0.49	0.49	0.00	0.03	1.00
$[HO\cdots R\cdots F]^-$	0.53	0.45	0.00	0.02	0.84
$[HO\cdots R\cdots \underline{CN}]^-$	0.41	0.49	0.11	0.00	1.20

Table 3.4.3 (continued)

$[\text{N}\cdots\text{R}\cdots\text{X}]^-$	a^2	b^2	c^2	d^2	$-\frac{b^2}{a^2}$
$[\text{HO}\cdots\text{R}\cdots\text{SH}]^-$	0.37	0.42	0.22	0.00	1.14
$[\text{HO}\cdots\text{R}\cdots\text{Cl}]^-$	0.50	0.29	0.21	0.00	0.59
$[\text{NC}\cdots\text{R}\cdots\text{H}]^-$	0.30	0.44	0.27	0.00	1.47
$[\text{NC}\cdots\text{R}\cdots\text{OH}]^-$	0.49	0.41	0.11	0.00	0.83
$[\text{NC}\cdots\text{R}\cdots\text{F}]^-$	0.51	0.36	0.13	0.00	0.71
$[\text{NC}\cdots\text{R}\cdots\text{CN}]^-$	0.34	0.34	0.32	0.00	1.00
$[\text{NC}\cdots\text{R}\cdots\text{SH}]^-$	0.31	0.34	0.36	0.00	1.10
$[\text{NC}\cdots\text{R}\cdots\text{Cl}]^-$	0.40	0.24	0.36	0.00	0.61
$[\text{HS}\cdots\text{R}\cdots\text{H}]^-$	0.28	0.41	0.31	0.00	1.50
$[\text{HS}\cdots\text{R}\cdots\text{OH}]^-$	0.42	0.37	0.22	0.00	0.88
$[\text{HS}\cdots\text{R}\cdots\text{F}]^-$	0.43	0.32	0.25	0.00	0.76
$[\text{HS}\cdots\text{R}\cdots\text{CN}]^-$	0.34	0.31	0.36	0.00	0.91
$[\text{HS}\cdots\text{R}\cdots\text{SH}]^-$	0.29	0.29	0.41	0.00	1.00
$[\text{HS}\cdots\text{R}\cdots\text{Cl}]^-$	0.38	0.23	0.39	0.00	0.59
$[\text{Cl}\cdots\text{R}\cdots\text{H}]^-$	0.20	0.53	0.27	0.00	2.66
$[\text{Cl}\cdots\text{R}\cdots\text{OH}]^-$	0.29	0.50	0.21	0.00	1.70
$[\text{Cl}\cdots\text{R}\cdots\text{F}]^-$	0.29	0.47	0.24	0.00	1.65
$[\text{Cl}\cdots\text{R}\cdots\text{CN}]^-$	0.24	0.40	0.36	0.00	1.64
$[\text{Cl}\cdots\text{R}\cdots\text{SH}]^-$	0.23	0.38	0.39	0.00	1.68
$[\text{Cl}\cdots\text{R}\cdots\text{Cl}]^-$	0.30	0.30	0.39	0.00	1.00

Table 3.4.4 Configuration analysis at the MP2' level.

$[\text{N}\cdots\text{R}\cdots\text{X}]^-$	a^2	b^2	c^2	d^2	$-\frac{b^2}{a^2}$
$[\text{H}\cdots\text{R}\cdots\text{H}]^-$	0.45	0.45	0.10	0.00	1.00
$[\text{H}\cdots\text{R}\cdots\text{NH}_2]^-$	0.55	0.42	0.03	0.00	0.76
$[\text{H}\cdots\text{R}\cdots\text{OH}]^-$	0.61	0.34	0.00	0.05	0.57
$[\text{H}\cdots\text{R}\cdots\text{F}]^-$	0.65	0.31	0.00	0.04	0.48
$[\text{H}\cdots\text{R}\cdots\text{NC}]^-$	0.68	0.28	0.00	0.04	0.42
$[\text{H}\cdots\text{R}\cdots\text{CCH}]^-$	0.47	0.39	0.14	0.00	0.83
$[\text{H}\cdots\text{R}\cdots\text{CN}]^-$	0.50	0.37	0.13	0.00	0.76
$[\text{H}\cdots\text{R}\cdots\text{SH}]^-$	0.48	0.35	0.17	0.00	0.73
$[\text{H}\cdots\text{R}\cdots\text{Cl}]^-$	0.60	0.26	0.14	0.00	0.44
$[\text{F}\cdots\text{R}\cdots\text{H}]^-$	0.31	0.65	0.00	0.04	2.09
$[\text{F}\cdots\text{R}\cdots\text{NH}_2]^-$	0.36	0.59	0.00	0.05	1.67
$[\text{F}\cdots\text{R}\cdots\text{OH}]^-$	0.42	0.51	0.00	0.07	1.21
$[\text{F}\cdots\text{R}\cdots\text{F}]^-$	0.47	0.47	0.00	0.07	1.00
$[\text{F}\cdots\text{R}\cdots\text{NC}]^-$	0.47	0.48	0.00	0.05	1.03
$[\text{F}\cdots\text{R}\cdots\text{CN}]^-$	0.40	0.59	0.00	0.01	1.49
$[\text{F}\cdots\text{R}\cdots\text{SH}]^-$	0.42	0.56	0.03	0.00	1.35
$[\text{F}\cdots\text{R}\cdots\text{Cl}]^-$	0.54	0.40	0.06	0.00	0.75
$[\text{HO}\cdots\text{R}\cdots\text{H}]^-$	0.34	0.61	0.00	0.05	1.77
$[\text{HO}\cdots\text{R}\cdots\text{OH}]^-$	0.46	0.46	0.00	0.08	1.00
$[\text{HO}\cdots\text{R}\cdots\text{F}]^-$	0.51	0.42	0.00	0.07	0.83
$[\text{HO}\cdots\text{R}\cdots\text{CN}]^-$	0.42	0.56	0.00	0.01	1.33

Table 3.4.4 (continued)

$[\text{N}\cdots\text{R}\cdots\text{X}]^-$	a^2	b^2	c^2	d^2	$-\frac{b^2}{a^2}$
$[\text{HO}\cdots\text{R}\cdots\text{SH}]^-$	0.45	0.53	0.02	0.00	1.19
$[\text{HO}\cdots\text{R}\cdots\text{Cl}]^-$	0.57	0.40	0.04	0.00	0.71
$[\text{NC}\cdots\text{R}\cdots\text{H}]^-$	0.37	0.50	0.13	0.00	1.32
$[\text{NC}\cdots\text{R}\cdots\text{OH}]^-$	0.56	0.42	0.00	0.01	0.75
$[\text{NC}\cdots\text{R}\cdots\text{F}]^-$	0.59	0.40	0.00	0.01	0.67
$[\text{NC}\cdots\text{R}\cdots\text{CN}]^-$	0.41	0.41	0.17	0.00	1.00
$[\text{NC}\cdots\text{R}\cdots\text{SH}]^-$	0.40	0.39	0.21	0.00	0.98
$[\text{NC}\cdots\text{R}\cdots\text{Cl}]^-$	0.51	0.29	0.20	0.00	0.58
$[\text{HS}\cdots\text{R}\cdots\text{H}]^-$	0.35	0.48	0.17	0.00	1.37
$[\text{HS}\cdots\text{R}\cdots\text{OH}]^-$	0.53	0.45	0.02	0.00	0.84
$[\text{HS}\cdots\text{R}\cdots\text{F}]^-$	0.56	0.42	0.03	0.00	0.74
$[\text{HS}\cdots\text{R}\cdots\text{CN}]^-$	0.39	0.40	0.21	0.00	1.02
$[\text{HS}\cdots\text{R}\cdots\text{SH}]^-$	0.38	0.38	0.24	0.00	1.00
$[\text{HS}\cdots\text{R}\cdots\text{Cl}]^-$	0.46	0.32	0.22	0.00	0.69
$[\text{Cl}\cdots\text{R}\cdots\text{H}]^-$	0.26	0.60	0.14	0.00	2.27
$[\text{Cl}\cdots\text{R}\cdots\text{OH}]^-$	0.40	0.57	0.04	0.00	1.41
$[\text{Cl}\cdots\text{R}\cdots\text{F}]^-$	0.40	0.54	0.06	0.00	1.33
$[\text{Cl}\cdots\text{R}\cdots\text{CN}]^-$	0.29	0.51	0.20	0.00	1.73
$[\text{Cl}\cdots\text{R}\cdots\text{SH}]^-$	0.32	0.46	0.22	0.00	1.46
$[\text{Cl}\cdots\text{R}\cdots\text{Cl}]^-$	0.37	0.39	0.23	0.00	1.00

Tabke 3.4.5 Configuration analysis at the MP2 level.

$[\text{N}\cdots\text{R}\cdots\text{X}]^-$	a^2	b^2	c^2	d^2	$-\frac{b^2}{a^2}$
$[\text{H}\cdots\text{R}\cdots\text{H}]^-$	0.45	0.45	0.09	0.00	1.00
$[\text{H}\cdots\text{R}\cdots\text{NH}_2]^-$	0.60	0.38	0.02	0.00	0.63
$[\text{H}\cdots\text{R}\cdots\text{OH}]^-$	0.66	0.30	0.00	0.04	0.45
$[\text{H}\cdots\text{R}\cdots\text{F}]^-$	0.72	0.25	0.00	0.03	0.35
$[\text{H}\cdots\text{R}\cdots\text{NC}]^-$	0.71	0.24	0.00	0.05	0.34
$[\text{H}\cdots\text{R}\cdots\text{CCH}]^-$	0.46	0.38	0.17	0.00	0.82
$[\text{H}\cdots\text{R}\cdots\text{CN}]^-$	0.47	0.36	0.17	0.00	0.76
$[\text{H}\cdots\text{R}\cdots\text{SH}]^-$	0.51	0.34	0.15	0.00	0.67
$[\text{H}\cdots\text{R}\cdots\text{Cl}]^-$	0.62	0.26	0.12	0.00	0.41
$[\text{F}\cdots\text{R}\cdots\text{H}]^-$	0.25	0.72	0.00	0.03	2.89
$[\text{F}\cdots\text{R}\cdots\text{NH}_2]^-$	0.31	0.64	0.00	0.04	2.06
$[\text{F}\cdots\text{R}\cdots\text{OH}]^-$	0.39	0.55	0.00	0.06	1.40
$[\text{F}\cdots\text{R}\cdots\text{F}]^-$	0.48	0.48	0.00	0.05	1.00
$[\text{F}\cdots\text{R}\cdots\text{CN}]^-$	0.37	0.63	0.00	0.00	1.69
$[\text{F}\cdots\text{R}\cdots\text{SH}]^-$	0.37	0.61	0.02	0.00	1.65
$[\text{F}\cdots\text{R}\cdots\text{Cl}]^-$	0.48	0.47	0.05	0.00	0.96

to the reactant contribution is related to the exothermicity (or endothermicity) of the reaction. As the reaction becomes more exothermic, the TS comes early and the ratio b^2/a^2 becomes small (see Tables 3.4.4 and 3.4.5).

It is also possible to analyse the TS wavefunction in terms of reactant ion-molecule complex (Ψ_{rc}) and product ion-molecule complex (Ψ_{pc}). If Ψ_{rc} and Ψ_{pc} are written as

$$\Psi_{rc} = \alpha_1 \psi_1 + \alpha_2 \psi_3 + \alpha_3 \psi_5 \quad (3.4.9)$$

and

$$\Psi_{pc} = \beta_1 \psi_2 + \beta_2 \psi_3 + \beta_3 \psi_6 \quad (3.4.10)$$

then the TS wavefunction can be approximated as

$$\Psi_{TS} = \alpha \Psi_{rc} + \beta \Psi_{pc} + \lambda \psi_3 + \gamma \psi_4 \quad (3.4.11)$$

Using the integrated charges $Q_A(\Psi_{rc})$ and $Q_A(\Psi_{pc})$, see Table 3.4.6 and following the same arguments, the coefficients can be evaluated. The results obtained at the MP2 level are listed in Table 3.4.7. The results indicate that the reactant ion-molecule complex and the product ion-molecule complex still do not make equal contributions to the TS wavefunction. However, the contribution from configurations other than the reactant ion-molecule complex and the product ion-molecule complex is small. This indicates that upon the formation of the reactant or

Table 3.4.6 Integrated charges on N and X in ion-molecule complexes

 $\text{N}^{\cdot-} \cdots \text{RX}$ at the MP2 level (e).

$[\text{N}^{\cdot-} \cdots \text{RX}]$	$-Q_{\text{N}}$	$-Q_{\text{X}}$
$[\text{H}^{\cdot-} \cdots \text{RH}]$	0.975	0.048
$[\text{H}^{\cdot-} \cdots \text{RNH}_2]$	0.959	0.406
$[\text{H}^{\cdot-} \cdots \text{ROH}]$	0.946	0.548
$[\text{H}^{\cdot-} \cdots \text{RF}]$	0.927	0.633
$[\text{H}^{\cdot-} \cdots \text{RNC}]$	0.924	0.718
$[\text{H}^{\cdot-} \cdots \text{RCCH}]$	0.948	0.395
$[\text{H}^{\cdot-} \cdots \text{RCN}]$	0.931	0.444
$[\text{H}^{\cdot-} \cdots \text{RSH}]$	0.936	0.121
$[\text{H}^{\cdot-} \cdots \text{RCl}]$	0.911	0.339
$[\text{H}_2\text{N}^{\cdot-} \cdots \text{RH}]$	0.978	0.082
$[\text{HO}^{\cdot-} \cdots \text{RH}]$	0.985	0.087
$[\text{F}^{\cdot-} \cdots \text{RH}]$	0.986	0.079
$[\text{CN}^{\cdot-} \cdots \text{RH}]$	0.991	0.061
$[\text{HCC}^{\cdot-} \cdots \text{RH}]$	0.984	0.058
$[\text{NC}^{\cdot-} \cdots \text{RH}]$	0.988	0.053
$[\text{HS}^{\cdot-} \cdots \text{RH}]$	0.988	0.057
$[\text{Cl}^{\cdot-} \cdots \text{RH}]$	0.988	0.055

Table 3.4.7 Configuration analysis in terms of ion-molecule complexes at the MP2 level.

$[N \cdots R \cdots X]^-$	α^2	β^2	λ^2	γ^2	$-\frac{\beta^2}{\alpha^2}$
$[H \cdots R \cdots H]^-$	0.50	0.50	0.01	0.00	1.00
$[H \cdots R \cdots NH_2]^-$	0.59	0.37	0.00	0.04	0.63
$[H \cdots R \cdots OH]^-$	0.65	0.28	0.00	0.07	0.43
$[H \cdots R \cdots F]^-$	0.74	0.21	0.00	0.05	0.29
$[H \cdots R \cdots \underline{N}C]^-$	0.74	0.17	0.00	0.08	0.23
$[H \cdots R \cdots CCH]^-$	0.56	0.40	0.04	0.00	0.71
$[H \cdots R \cdots \underline{C}N]^-$	0.56	0.36	0.07	0.00	0.65
$[H \cdots R \cdots SH]^-$	0.58	0.35	0.08	0.00	0.60
$[H \cdots R \cdots Cl]^-$	0.73	0.22	0.05	0.00	0.30

product ion-molecule complex, the electron distribution is shifted such that R becomes more positively charged and X or N is more negatively charged, i.e. the contribution of ψ_3 to the reactant ion-molecule complex and the product ion-molecule complex is larger and as a result the interactions between N^- , RX and X^- , RN are enhanced.

The TS wavefunction can also be analyzed in terms of VB configurations. Substitution of eq. 3.4.4 into eq. 3.4.6, yields another set of equations

$$\left\{ \begin{array}{l} Q_X = c_1^2 Q_X(\psi_1) + c_2^2 Q_X(\psi_2) + c_3^2 Q_X(\psi_3) + c_4^2 Q_X(\psi_4) \\ Q_N = c_1^2 Q_N(\psi_1) + c_2^2 Q_N(\psi_2) + c_3^2 Q_N(\psi_3) + c_4^2 Q_N(\psi_4) \\ c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1 \end{array} \right. \quad (3.4.12)$$

Also by setting c_3^2 or $c_4^2 = 0$, it is possible to evaluate c_1^2 , c_2^2 , c_4^2 or c_3^2 . In all the cases studied, Q_X and Q_N are more negative than -0.5. Hence, $c_3^2 = 0$ is not reasonable, and therefore in all the cases c_4^2 is set equal to zero. The results obtained at the MP2 level are shown in Table 3.4.8. From the form of the TS wavefunction eq. 3.4.4 or eq. 3.4.12, it is apparent that if ψ_1 and ψ_2 make the same contribution to the TS, then the charges on N and X in the TS will be approximately equal. Conversely, if the charges are equal, $c_1^2 \approx c_2^2$. The results in Table 3.4.8 show that in some cases, c_1^2 and c_2^2 are equal while in some others they are quite close (compare with the difference between a^2 , b^2 and α^2 , β^2) and in still other cases, c_1^2 and c_2^2 are quite different. Thus, the assumption that the TS occurs in the vicinity of the

Table 3.4.8 Configuration analysis in terms of VB configurations at the MP2 level.

$[N\cdots R\cdots X]^-$	c_1^2	c_2^2	c_3^2	c_4^2
$[H\cdots R\cdots H]^-$	0.48	0.48	0.03	0.00
$[H\cdots R\cdots NH_2]^-$	0.40	0.40	0.20	0.00
$[H\cdots R\cdots OH]^-$	0.36	0.36	0.28	0.00
$[H\cdots R\cdots F]^-$	0.32	0.30	0.38	0.00
$[H\cdots R\cdots \underline{NC}]^-$	0.29	0.30	0.40	0.00
$[H\cdots R\cdots CCH]^-$	0.35	0.40	0.25	0.00
$[H\cdots R\cdots \underline{CN}]^-$	0.32	0.38	0.30	0.00
$[H\cdots R\cdots SH]^-$	0.51	0.36	0.12	0.00
$[H\cdots R\cdots Cl]^-$	0.49	0.28	0.24	0.00
$[F\cdots R\cdots H]^-$	0.30	0.32	0.38	0.00
$[F\cdots R\cdots NH_2]^-$	0.25	0.30	0.45	0.00
$[F\cdots R\cdots OH]^-$	0.25	0.28	0.47	0.00
$[F\cdots R\cdots F]^-$	0.24	0.24	0.52	0.00
$[F\cdots R\cdots \underline{CN}]^-$	0.25	0.25	0.49	0.00
$[F\cdots R\cdots SH]^-$	0.37	0.24	0.38	0.00
$[F\cdots R\cdots Cl]^-$	0.38	0.19	0.44	0.00

intersection point of the two VB configurations ψ_1 and ψ_2 is better than the assumption that the TS occurs in the vicinity of the intersection point of the reactant and product configurations, or of the intersection point of the configurations corresponding to the reactant ion-molecule complex and product ion-molecule complex.

In most cases ψ_3 makes a large contribution to the TS and is responsible for the large negative charges on N and X. As mentioned previously, the charges on N and X differ from system to system. What are the factors responsible for the difference? In the ground state, electronegativity plays a leading role in affecting the charge on X. At the TS, the electronegativity is responsible for the charge difference on N and X. Thus, all things being equal, the more electronegative N or X, the greater the negative charge on N or X. For example, the reactions $N = X = OH$ and $N = X = F$ are thermoneutral reactions and ψ_4 makes similar contributions to the TS ($d^2 = 0.08$ and 0.07 , respectively at the MP2' level). The charge difference between OH and F is a result of the electronegativity difference. The more electronegative atom F has more negative charge (0.764 compared with 0.708 on OH, see Table 3.4.2). However, the TS has contributions not only from reactant and product configurations but also from the VB configurations ψ_3 and ψ_4 . The contributions from the latter will certainly affect the charge on N and X. Therefore, all things being equal, the larger contribution of ψ_3 to the TS will result in a large charge on N and X. For example, H and SH have similar electronegativities. For symmetric reactions $N = X = H$ and $N = X = SH$, ΔE_t° is zero. Since the latter has a larger ψ_3 contribution to the TS ($c^2 = 0.24$ at the MP2' level), there are larger charges on the

SH groups at the TS, $Q_N = Q_X = 0.618$, whereas, for the former, $c^2 = 0.10$, $Q_N = Q_X = 0.520$. Finally, the charges on N and X are related to the position of the TS along the reaction coordinate. At the TS, regardless of the difference in electronegativity between N and X, the charges on N and X can still be equal. This is explained by the fact that the position of the TS is not in the middle (i.e. $\Delta E_t^\circ \neq 0$). For example, the reaction with N = H and X = OH is exothermic and the TS comes early. Thus, fewer electrons are shifted away from H and also fewer electrons are transferred to OH. Therefore, even though H has a smaller electronegativity than OH, it bears negative charge comparable to that of OH. The three factors discussed above are illustrated by Fig. 3.4.1-3.4.4. Fig. 3.4.1 shows the charge development $\Delta Q_N = |Q_N - Q_N(\psi_p)|$, N = H, as a function of the reaction energy ΔE_t° . As ΔE_t° becomes more negative, the TS resembles the reactant more, and there is greater charge transfer from the TS to the product. Fig. 3.4.2 shows the charge development on X in the same reactions, $\Delta Q_X = |Q_X - Q_X(\psi_r)|$. Since the electronegativities of X are not equal, the c^2 values are not the same and the charge development is not related to ΔE_t° by a simple linear relationship. Rather, it appears that these X fall within three groups according to their electronegativities. Within each group the charge development is related to ΔE_t° . Negative ΔE_t° is associated with an early TS and the transition structure resembles the reactants. Hence small charge development on X is observed in going from reactant to the TS and ΔQ_X is small. Fig. 3.4.3 and 3.4.4 show the corresponding plots for reactions with N = F. They exhibit the same pattern, although Fig. 3.4.3 shows a better correlation than that of Fig. 3.4.1. This is explained by

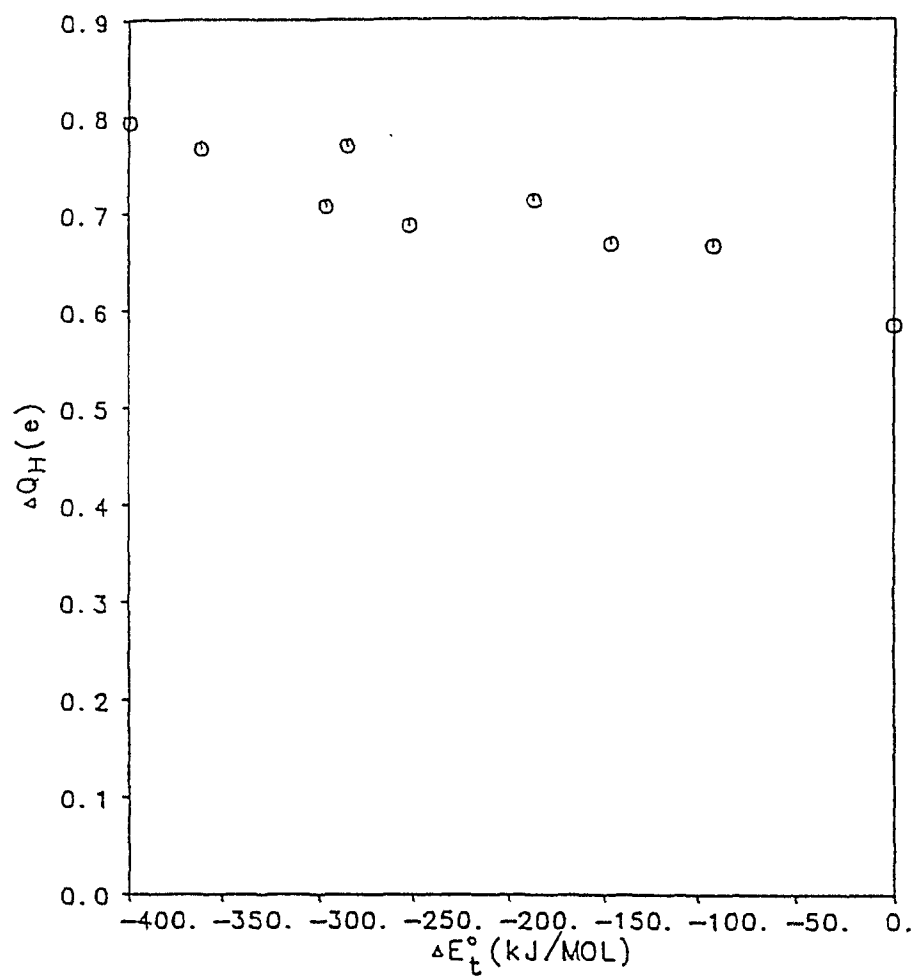


Figure 3.4.1 Charge development on H as a function of ΔE_t^0 for the reactions $\text{H}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_4 + \text{X}^-$ (MP2 results).

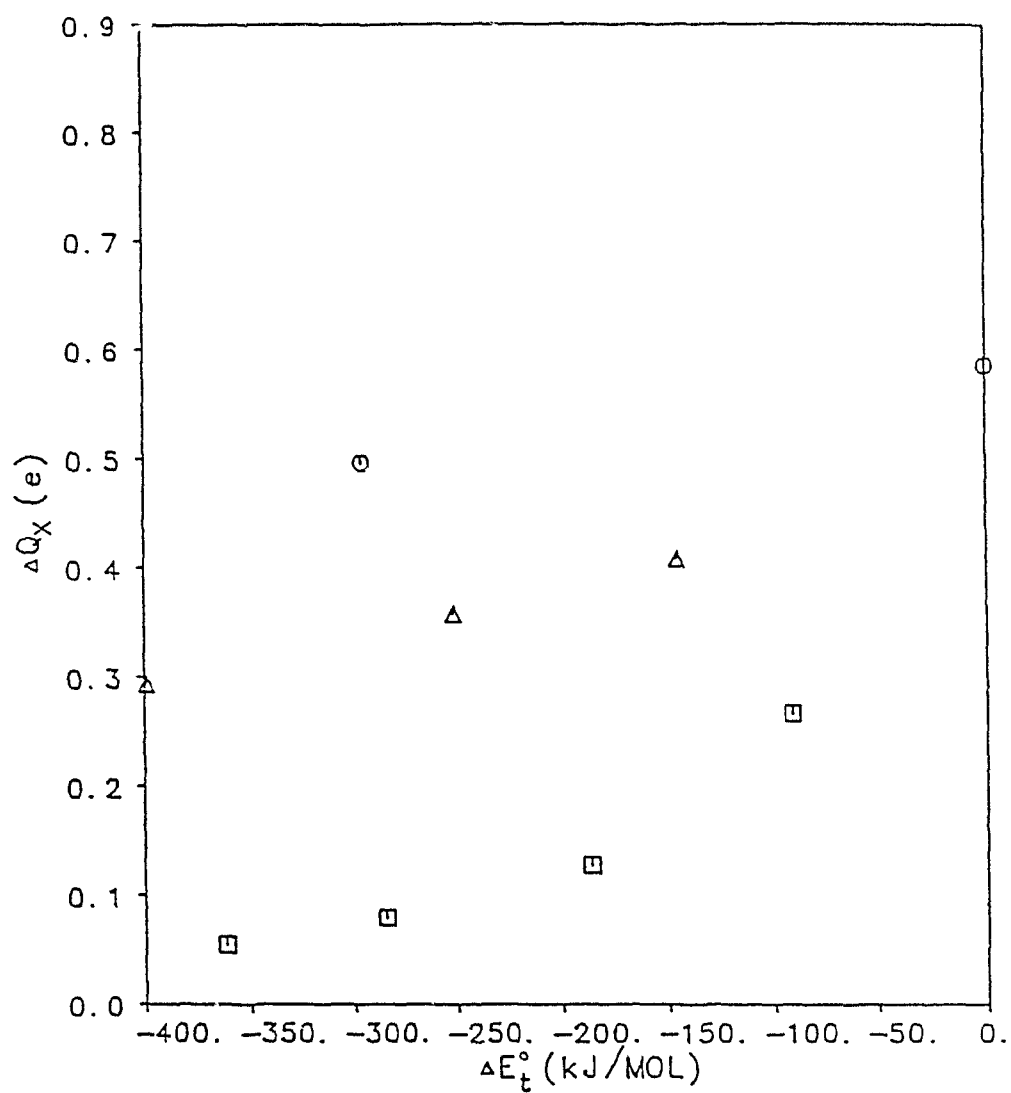


Figure 3.4.2 Charge development on X as a function of ΔE_t° for the reactions $H^- + CH_3X \rightarrow CH_4 + X^-$.

a) X = H, SH (O);

b) X = CCH, $\underline{C}N$ and Cl (Δ);

c) X = NH_2 , OH, F and $\underline{N}C$ ($\square$).

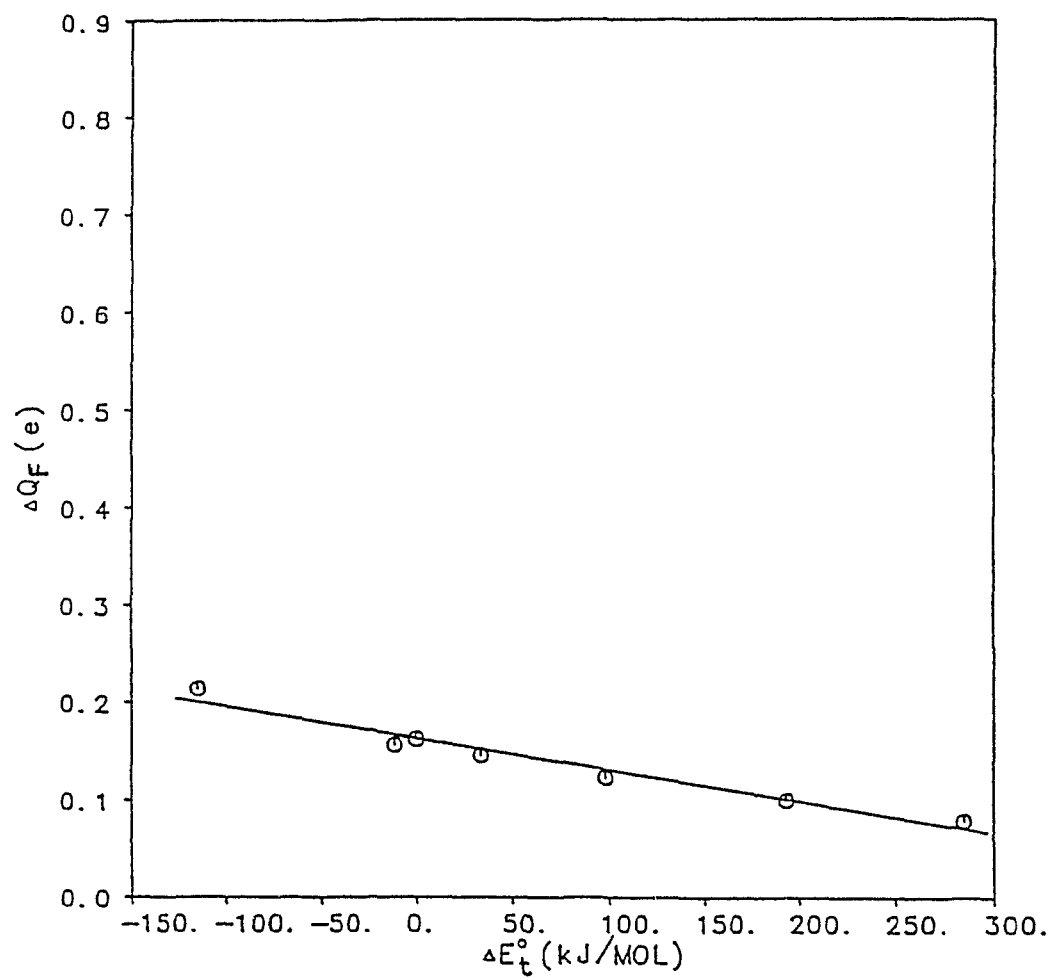


Figure 3.4.3 Charge development on F as a function of ΔE_t° , for the reactions $F^- + CH_3X \rightarrow CH_3F + X^-$.

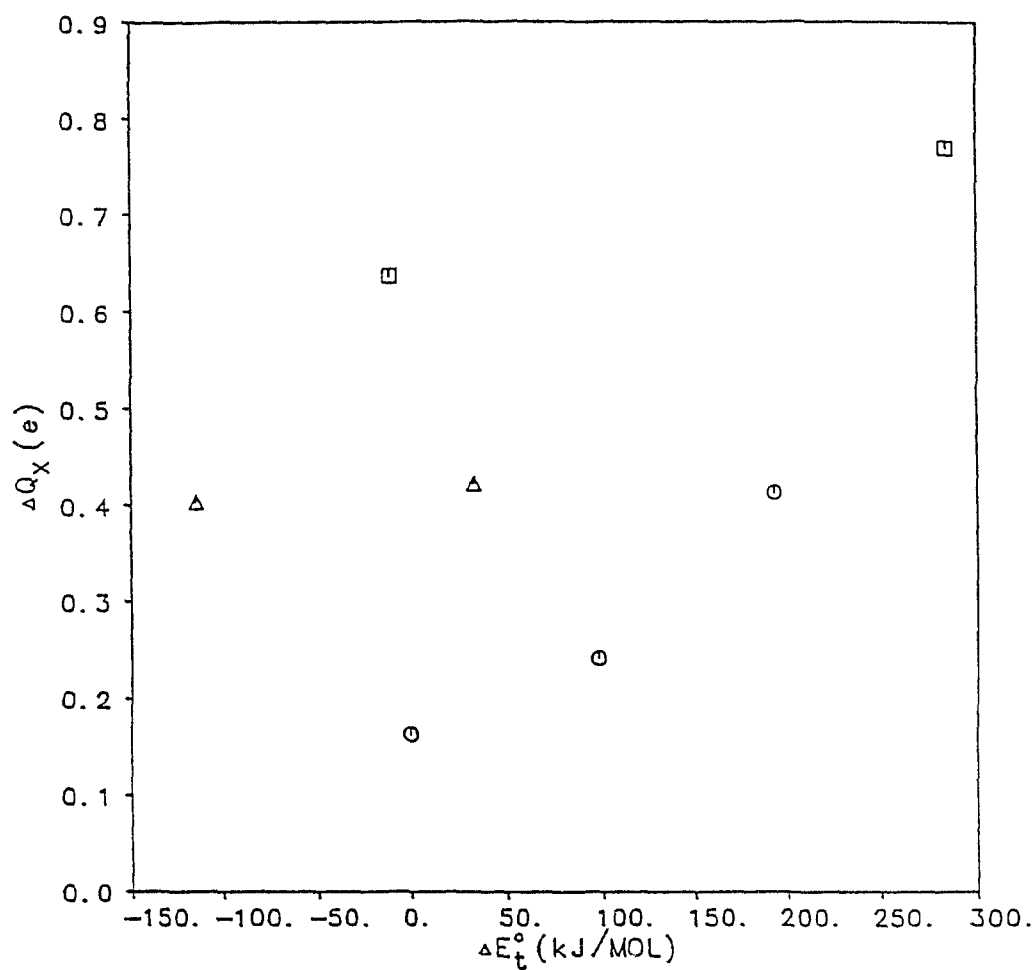


Figure 3.4.4 Charge development on X as a function of ΔE_t° for the

reactions $\text{F}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_3\text{F} + \text{X}^-$.

a) X = H and SH ($\square$);

b) X = $\underline{\text{CN}}$ and Cl (Δ);

c) X = NH_2 , OH and F ($\circ$).

the fact that for reactions with $N = F$, the contributions from ψ_3 and ψ_4 are all relatively small.

In summary for S_N2 reactions the assumption that the TS occurs in the vicinity of the two VB configurations, ψ_1 and ψ_2 , generally holds at the MP2 level. A shift of the transition state away from the equal contribution point is caused by the exothermicity of the reaction and more importantly by the different bonding character in C-N and C-X bonds. The charge development on X or N in the TS is related to the electronegativity of X or N, the electronic structure of the TS and the exothermicity of the reaction. For those X or N which have similar electronegativities and TS electronic structures, the charge transfer is related to the exothermicity of the reaction.

3.5 Mulliken Population Analysis and the Charge Integration Method

As discussed previously, the charge distribution in the transition state has great significance for understanding the reaction process and for conceptualizing the transition state. The distribution of charge in molecular systems is also important for molecular structure and reactivity. The description of the charge distribution is undoubtedly a primary goal of any electronic structure theory. One of the most widely used charge distribution analysis methods is Mulliken's population analysis method (MPA). Unfortunately, it is also the most widely criticized method.⁴⁹ Mulliken populations can have unphysical negative values and the method is unduly sensitive to the basis set. Furthermore, even with the same electron distribution the result is not unique since it varies with the unitary transformation. The molecular structure

theory proposed by Bader and co-workers gives a unique definition of an atom in the molecule and a unique charge partitioning scheme.¹ In this section, the charges obtained by both methods are compared and the difference is explained. The systems reported in this section not only include the S_N2 reactions reported in this chapter, but also contain some binary fluoride molecules. For the latter, [5s4p]* and [6s5p]* contracted basis sets were used respectively for first-row and second-row atoms.⁵⁰ The calculations were done at the experimental geometries⁵¹ in order to economize on computer time.

The charges on F in AF_n and X in CH_3X obtained by MPA and integration of the electron density over atomic basins are plotted against each other in Fig. 3.5.1. The atoms in molecules (AIM) method usually yields a more negative charge than the MPA method. The charges on the entering nucleophile (Q_N) and on the leaving group (Q_X) in the TS are compared in Fig. 3.5.2. Once again, the AIM method usually results in larger net charges.

Proinov *et al.*⁵² proposed a definition of the MO-LCAO effective atomic charge, based on the concept of the topological atom. Using this definition, the MPA and AIM methods can be compared directly.

Proinov *et al.* have shown that the LCAO representation of the atomic electron occupancy, defined via the electron occupancy of the corresponding topological atom in the molecule, is

$$N(A) = \sum_{a \in A} \tilde{q}(Aa) \int_A \phi_{Aa}^2(\mathbf{r}) d\mathbf{r} \quad (3.5.1)$$

where the orbital occupancies of the topological atom are

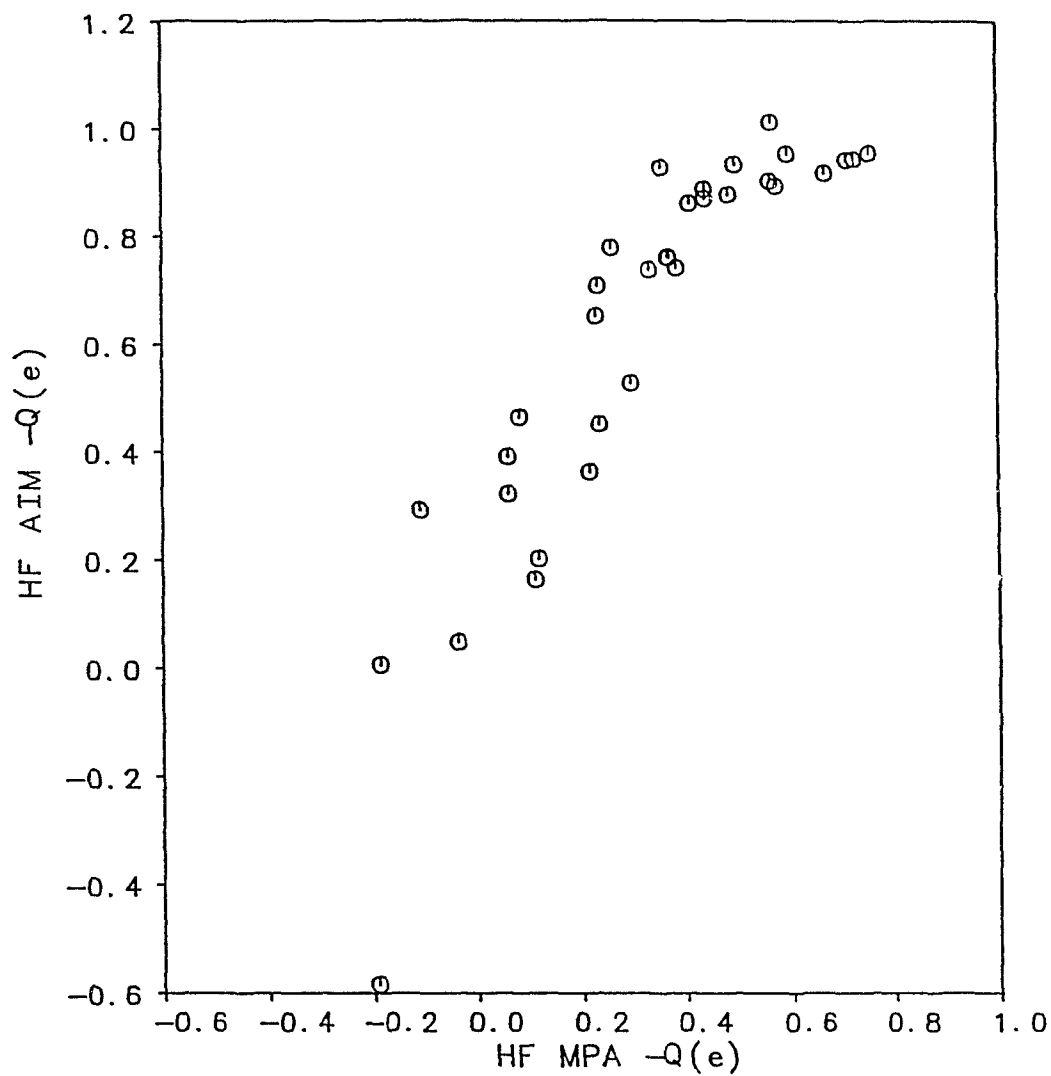


Figure 3.5.1 Comparison of charges on F in AF_n and X in CH_3X as obtained by the MPA and AIM methods.

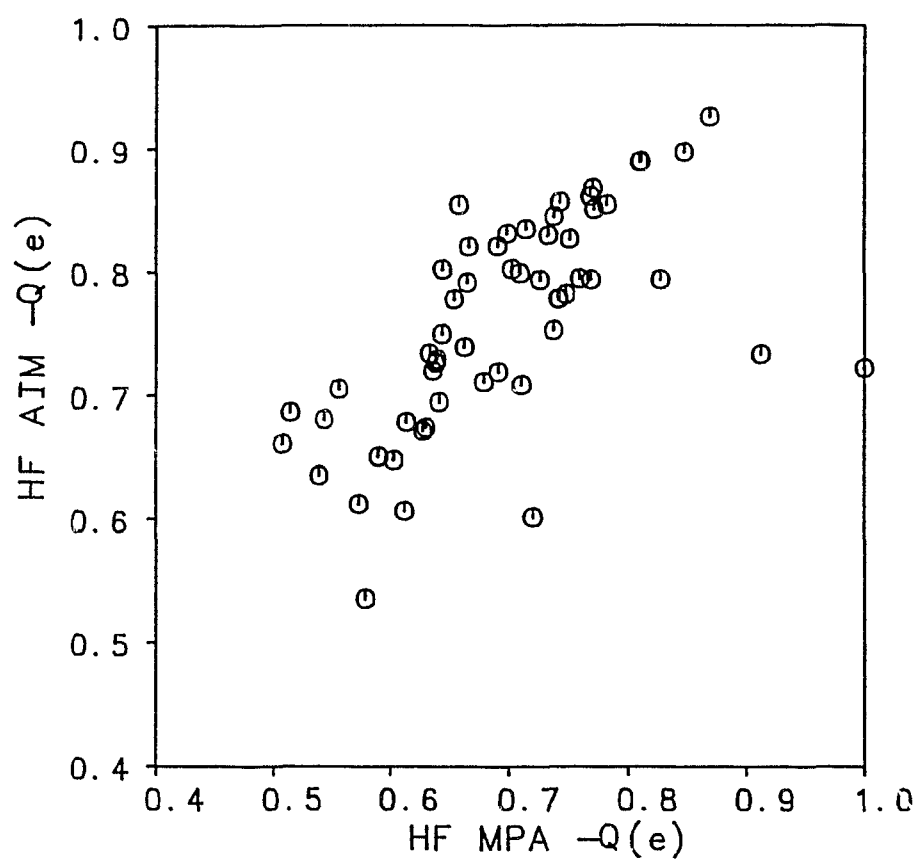


Figure 3.5.2 Charges on N and X in the TS as obtained by the MPA and AIM methods.

$$\tilde{q}(Aa) = P\left(\frac{Aa}{Aa}\right) + 2 \sum_{\substack{B, b \\ B \neq A}} S_{Aa, Bb} P\left(\frac{Bb}{Aa}\right) + \sum_{\substack{Bb, B'b' \\ B, B' \neq A}} S_{Aa, Bb} S_{Aa, B'b'} P\left(\frac{Bb}{B'b'}\right) \quad (3.5.2)$$

In eq. 3.5.2 $P\left(\frac{Aa}{Aa}\right)$ are elements of the density matrix and $S_{Aa, Bb}$ are elements of the overlap matrix. Atoms are labelled as A, B, and AO's are labelled as a, b, The equation

$$N(A) = \sum_{a \in A} q(Aa) \quad (3.5.3)$$

where

$$q(Aa) = P\left(\frac{Aa}{Aa}\right) + \sum_{\substack{B, b \\ B \neq A}} S_{Aa, Bb} P\left(\frac{Bb}{Aa}\right) \quad (3.5.4)$$

contains the expression for the Mulliken gross atomic population as a special case. By comparison of eq. 3.5.1 with 3.5.3, it follows that the Mulliken population analysis emerges as an approximation to the electron occupancy of the topological atom. The topological occupancies $\tilde{q}(Aa)$ are quadratic functions of the overlap integrals, whereas Mulliken orbital occupancies are linear functions of the overlap integrals. As noted by Proinov *et al.*,⁵² the linear two-center contribution to $\tilde{q}(Aa)$ is twice as large as the corresponding contribution to $q(Aa)$. In contrast to the equal, but arbitrary, sharing of the two-center overlap term in MPA, an appropriate sharing of the LCAO charge density is achieved by means of the topological weight factors appearing in eq. 3.5.1

$$\int_A \psi_{Aa}^2(\mathbf{r}) d(\mathbf{r}) = F_{Aa} < 1 \quad (3.5.5)$$

The weight factor F_{Aa} is directly related to the topological definition of an atom. For two atoms at infinite separation, the interatomic surface is at infinity. Hence, the integration (eq. 3.5.5) is carried out to infinity. Thus, $F_{Aa} = 1$ for any orbital φ_{Aa} and there is no sharing of electrons between the two atoms. In the case of two directly bonded atoms, the interatomic surface passes through the bond critical point and it is apparent that the size of an atom is related to the position of the bond critical point. Furthermore, the distance between an atom and its bond critical point is related to the relative electronegativity of the two directly bonded atoms.⁵³ The more electronegative the atom the greater the critical radius, (see Table 3.5.1.) Furthermore, the more electronegative atom has a more contracted density distribution. The result is that the more electronegative atom has a larger weight factor and the two-center MO-LCAO electron density is not equally shared by the bonded atoms but rather the more electronegative one has the larger share. In the Mulliken population analysis, the weight factor does not exist and the two-center MO-LCAO electron density is assumed to be equally shared between the two atoms. As a result, the less electronegative atom is assigned more electrons than it should be, while, the more electronegative atom is assigned fewer electrons than it should be. Therefore, the MPA method usually yields smaller net charges than the integration method.

Proinvo *et al.* have pointed out that, in general, $\tilde{q}(Aa) > q(Aa)$ for any orbital φ_{Aa} . However, in the final result for the effective atomic charge (eq. 3.5.1), this inequality is compensated for by the reducing effect of the weight factor. The present calculations indicate that this

Table 3.5.1 Critical radii of binary fluorides (a.u.).

AF_n	r_{C-A}^a	r_{C-F}^b
LiF	1.138	1.817
BeF ₂	0.962	1.739
BF ₃	0.826	1.643
CF ₄	0.799	1.695
NF ₃	1.122	1.457
OF ₂	1.272	1.384
NaF	1.682	1.957
MgF ₂	1.492	1.853
AlF ₃	1.330	1.751
SiF ₄	1.221	1.715
PF ₃	1.175	1.775
SF ₂	1.160	1.849
ClF	1.259	1.818

Table 3.5.1 (continued)

AF	r_{C-A} (a. u.)	r_{C-F} (a. u.)
BeF	0.920	1.652
BF	0.808	1.578
CF	0.762	1.641
NF	0.979	1.510
OF	1.162	1.344
MgF	1.479	1.828
AlF	1.348	1.778
SiF	1.255	1.771
PF	1.196	1.809
SF	1.167	1.858

^a Distance between atom A and AF bond critical point.

^b Distance between atom F and AF bond critical point.

compensation factor is not big enough to make the results obtained by the two methods comparable. In some cases there is a fortuitous cancellation of errors. It is well documented that the HF method overestimates the importance of ionic character,⁵⁴ whereas, the MPA method underestimates the ionic character. The results obtained at the HF MPA level are compared with the results obtained by the MP2 AIM method in Fig. 3.5.3 and by the HF AIM in Fig. 3.5.4. The agreement with the MP2 AIM is better than with the HF AIM. Nevertheless, it is difficult to find a general relationship between the MPA and AIM results except the qualitative statement that MPA underestimates the ionic character and usually yields smaller net charges.

3.6 Comparison of Computational Methods

There have been substantial studies of ground state systems and much information is available in the literature. For the study of transition states greater computer time is usually involved and in order to make the study affordable, quite often, the electron correlation calculations are carried out at the geometries optimized at a lower level. In this section, we will report the effect of geometry optimization on calculated energies and charge distributions.

The ground state bond lengths C-X (in CH_3X) optimized by the RHF and MP2 methods are shown in Table 3.6.1 together with experimental bond lengths.^{51b} As usual, the MP2 calculations show a better agreement with the experimental results. The difference between the RHF and MP2, however, is quite small (Fig. 3.6.1)

The calculated dipole moments for the ground states are shown in

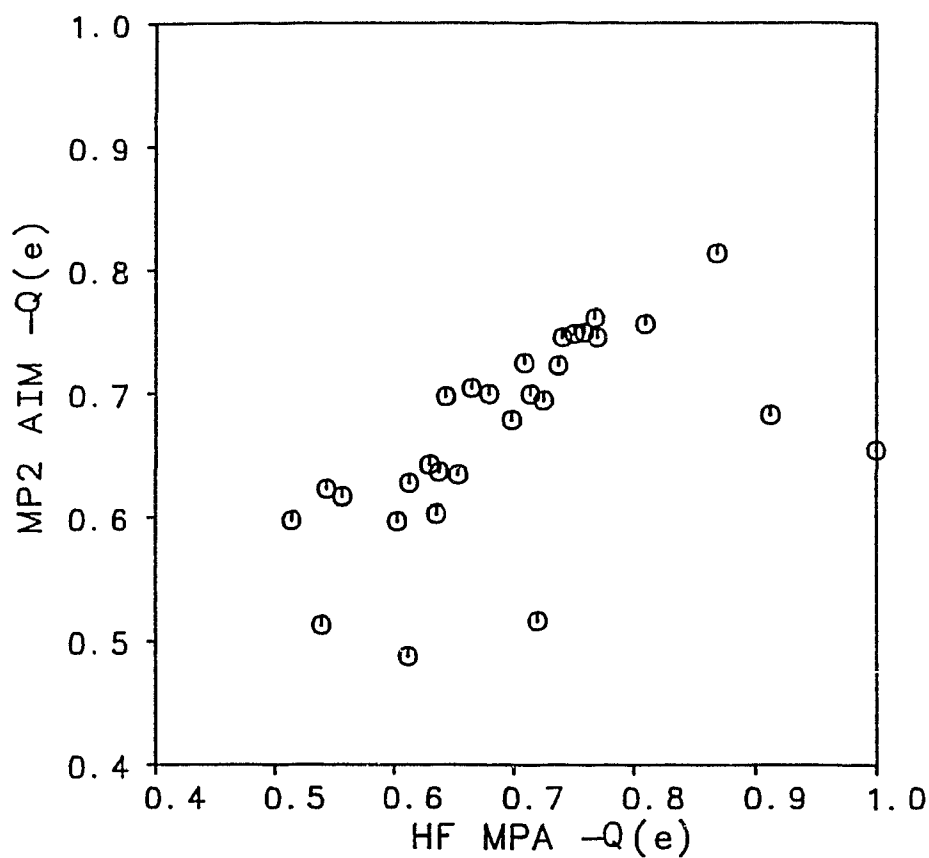


Figure 3.5.3 Comparison of Mulliken Population Analysis charges obtained at the HF level with the integration results obtained at the MP2 level.

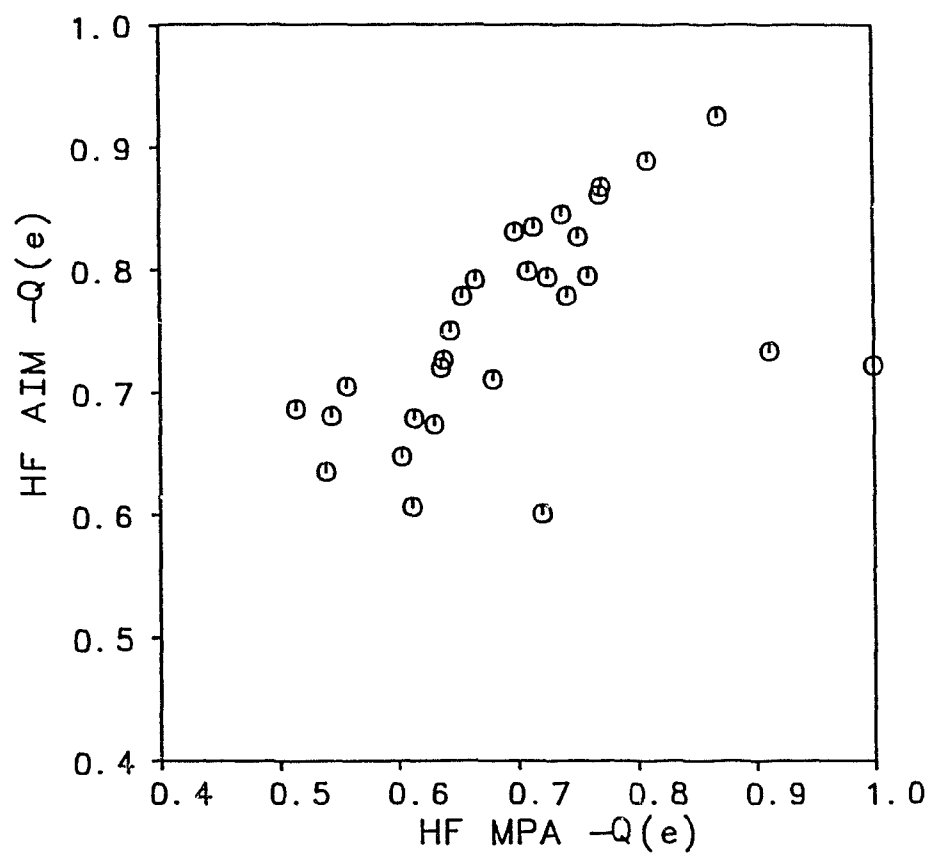


Figure 3.5.4 Comparison of the charges obtained by the MPA and AIM methods.

Table 3.6.1 C-X bond length in CH_3X (Å).

CH_3X	$R_{\text{C-X}}$		
	RHF	MP2	EXPT
CH_3H	1.084	1.091	1.094
CH_3NH_2	1.452	1.464	1.471
CH_3OH	1.401	1.429	1.425
CH_3F	1.371	1.406	1.382
CH_3NC	1.423	1.425	1.424
CH_3CCH	1.469	1.462	1.458
CH_3CN	1.469	1.462	1.458
CH_3SH	1.818	1.815	1.814
CH_3Cl	1.786	1.779	1.785

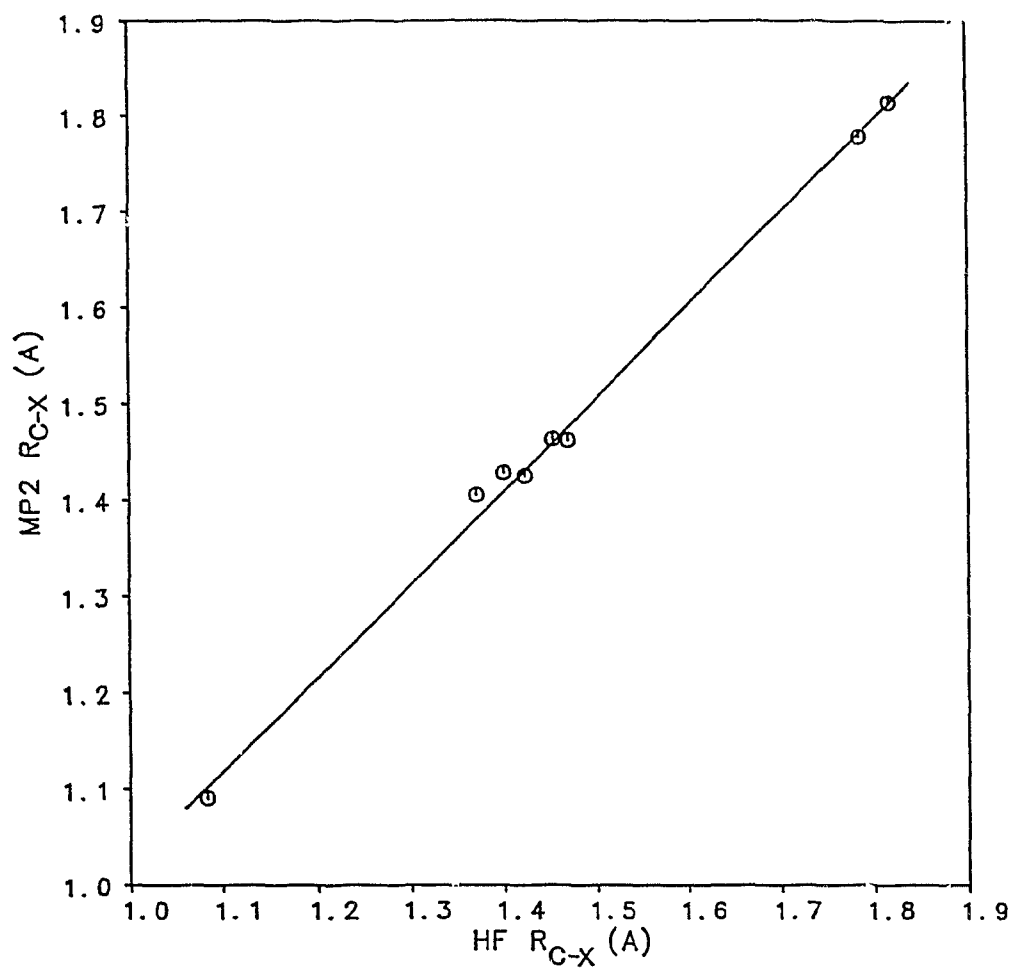


Figure 3.6.1 Comparison of the R_{C-X} bond length in CH_3X as calculated by the HF and MP2 methods.

Table 3.3.5. The RHF method results in dipole moments which are about 10% larger than the experimental values. The MP2' and MP2 results are very similar.

The integrated charges on X in the ground states are provided in Table 3.4.1 and here again, a larger difference between the RHF and MP2 results than between the MP2' and MP2 results is observed. The RHF method yields a larger negative charge on X. This is consistent with the tendency of the HF method to overestimate the importance of ionic character.

The TS bond lengths, R_{C-N} and R_{C-X} , obtained at the RHF and MP2 levels are compared in Fig. 3.6.2 (see also Table 3.3.6). Compared to the ground states, larger differences in bond lengths are observed. The RHF method usually gives a longer bond length. Table 3.3.7 provides the critical point values calculated at the RHF, MP2' and MP2 levels. The RHF method gives the smallest electron density at the bond critical point and the longest critical radius. The MP2' yields a electron density larger than that of RHF and smaller than that of MP2. Similarly, the MP2' critical radius is generally longer than that of MP2 and shorter than that of RHF.

The integrated charges on N and X in the TS are compared in Fig. 3.6.3-3.6.5. The charges obtained at the RHF level are always the most negative ones (Fig. 3.6.3-3.6.4). The MP2' method lowers the charge on N and X similarly, Fig. 3.6.4. The MP2 method lowers the charge on N and X unequally. Depending on the electronegativity of N and X, MP2 lowers the charge on the more electronegative group to a larger extent than on the less electronegative group (Fig. 3.6.3 and Fig. 3.6.5).

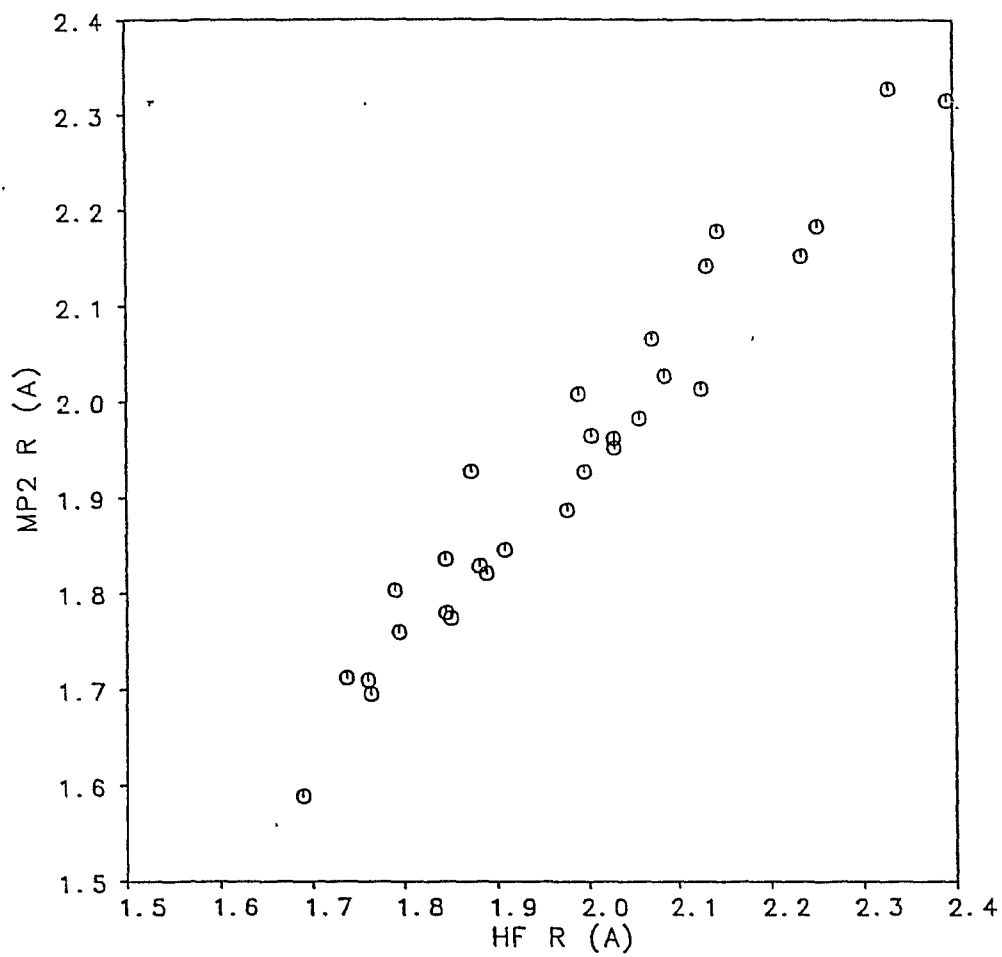


Figure 3.6.2 Comparison of the TS bond lengths R_{C-N} and R_{C-X} obtained at the HF and MP2 levels.

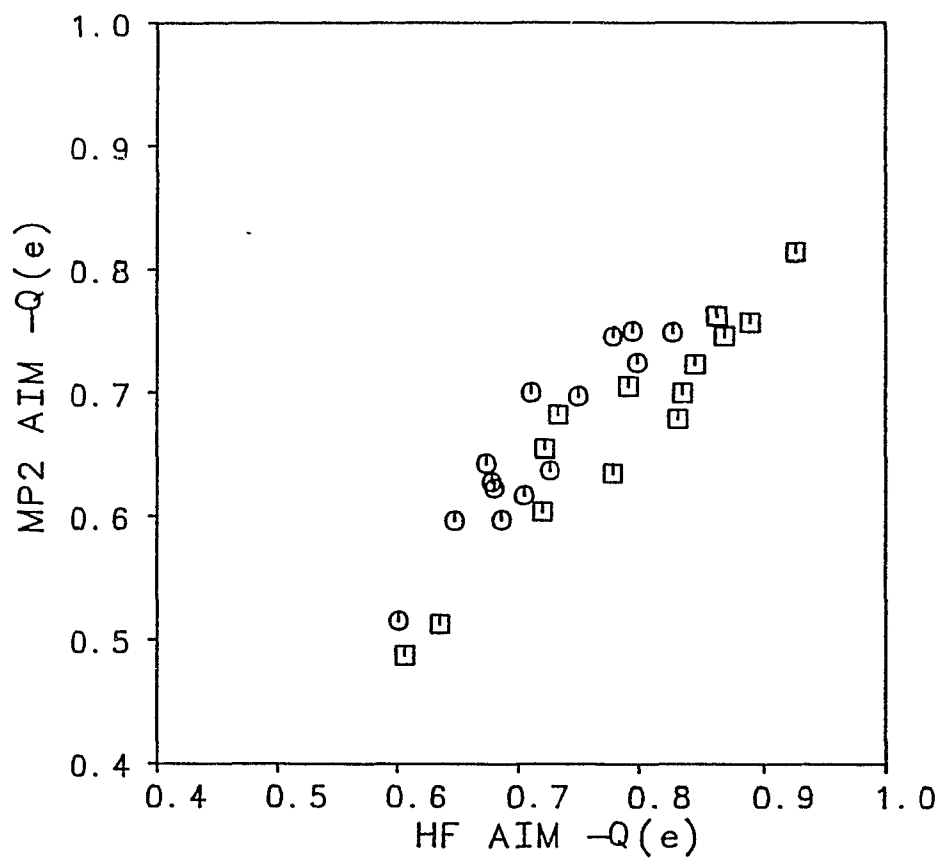


Figure 3.6.3 Comparison of integrated charges at the HF and MP2 levels.

□ is the more electronegative group between N and X,

O indicates the less electronegative group.

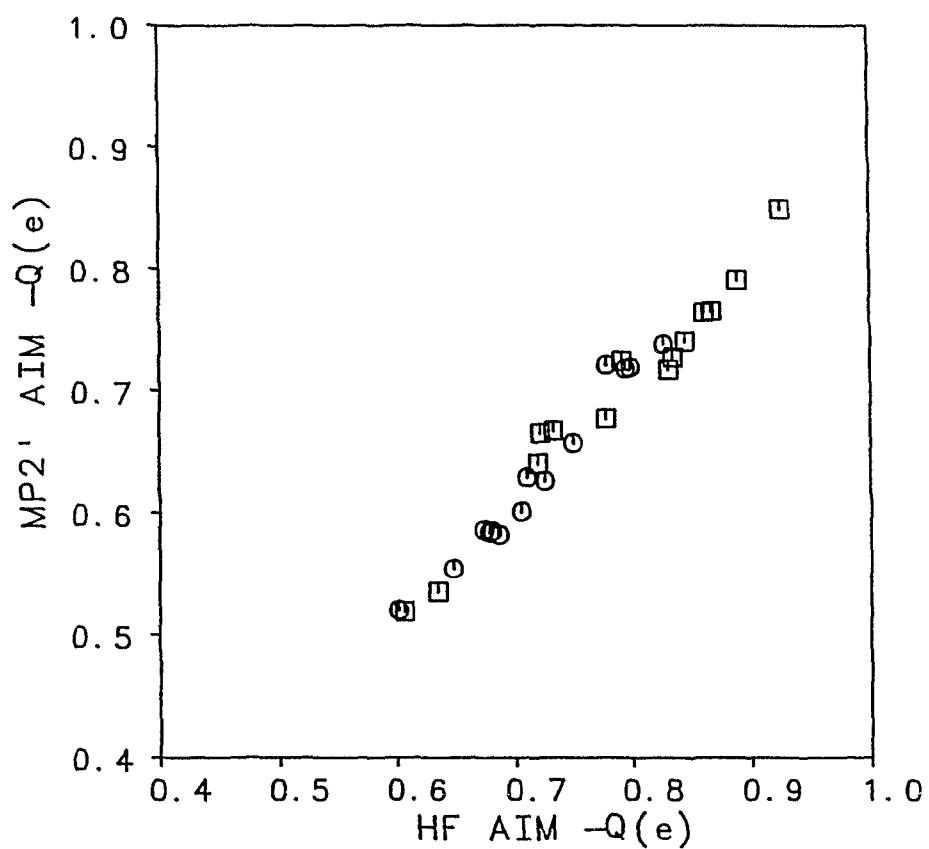


Figure 3.6.4 Comparison of integrated charges obtained at the HF and MP2' levels. □ indicates the more electronegative group between N and X, ○ indicates the less electronegative group.

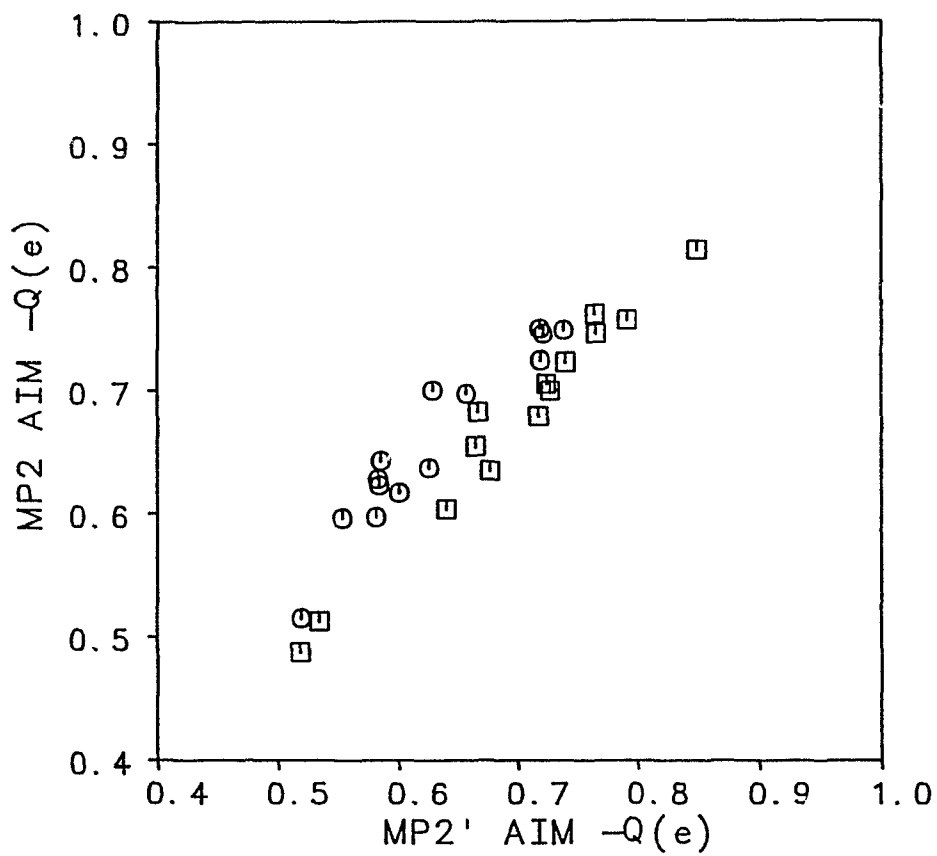


Figure 3.6.5 Integrated charges on N and X obtained at the MP2' and MP2 levels. □ indicates more electronegative group, O indicates the less electronegative group.

The configuration analysis results obtained at the RHF level (Table 3.4.3) have a large contribution from ψ_3 (c^2 is large). The contributions from ψ_3 and ψ_4 calculated at the MP2' and MP2 levels are usually small (Tables 3.4.4-3.4.5) and show the same trend. The large contribution of ψ_3 at the RHF level is a result of overestimating the importance of ionic character.

Various energies defined in eq. 3.3.2-3.3.7 are compared in Fig. 3.6.6-3.6.13. Fig. 3.6.6-3.6.9 compare the energies calculated at the RHF and MP2 levels. Fig. 3.6.10-3.6.13 compare the energies calculated at the MP2' and MP2 level. The RHF energy barriers ΔE_c^b and ΔE^b are usually larger than the MP2 results, while the RHF ΔE_c° and ΔE_t° are less exothermic than the MP2 values. The energies calculated at the MP2' and MP2 levels correlate well (Fig. 3.6.10-3.6.13).

In summary, geometries optimized by the RHF and MP2 methods are closer to each other in the ground state than in the transition state. This is understandable in light of the fact that the single determinant wave function gives a good description of the equilibrium geometry. Since the difference between the MP2' and MP2 ground state results is mainly caused by the difference in the geometry, the MP2' and MP2 calculations yield similar results (see dipole moments in Table 3.3.5 and integrated charges on X in Table 3.4.1). However, in the TS the MP2' results are not close to the MP2 results (see charges on X and N in Table 3.4.2 and critical point values in Table 3.3.7). Nevertheless, for properties which involve more than one state, for example energy differences and configuration analysis, the MP2' results are comparable with the MP2 results despite the significant differences in geometries.

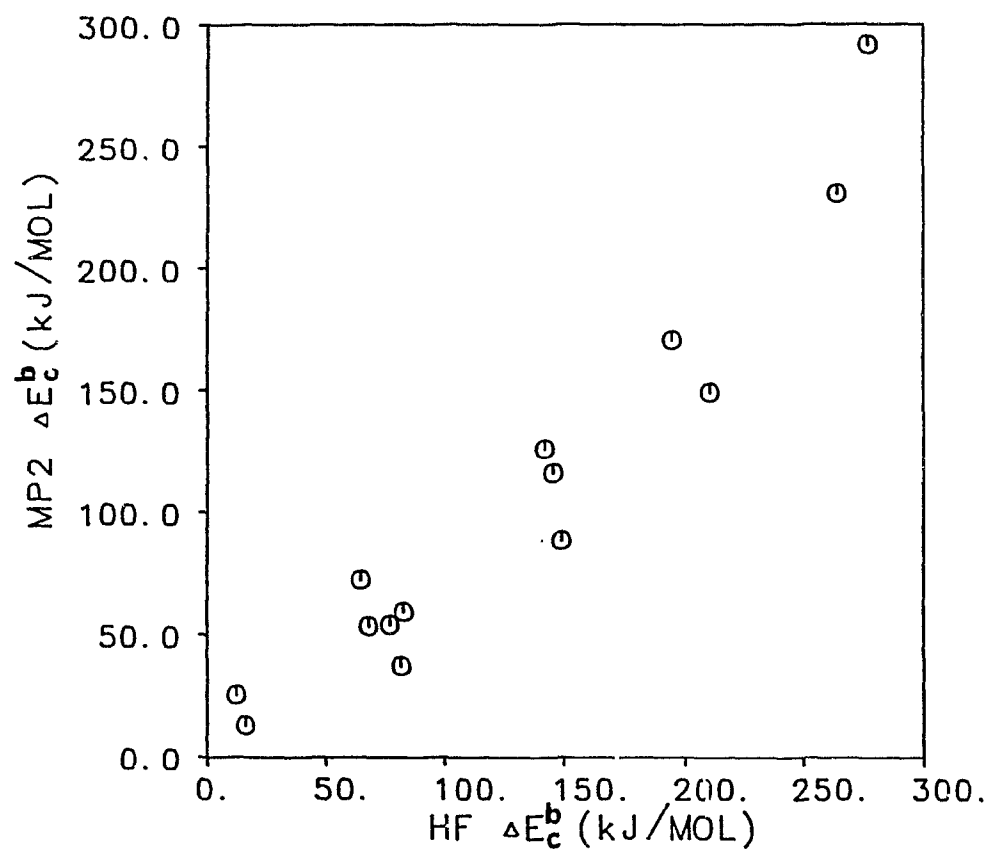


Figure 3.6.6 Comparison of ΔE_c^b obtained at the HF and MP2 levels.

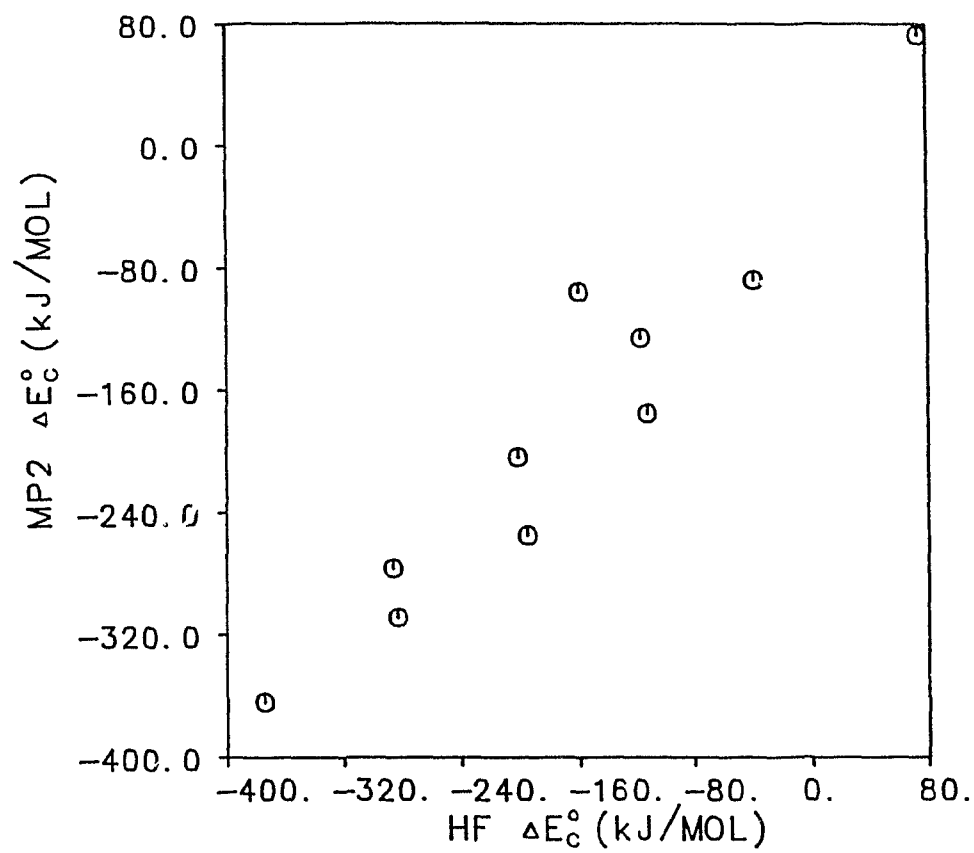


Figure 3.6.7 Comparison of ΔE_c^0 obtained at the HF and MP2 levels.

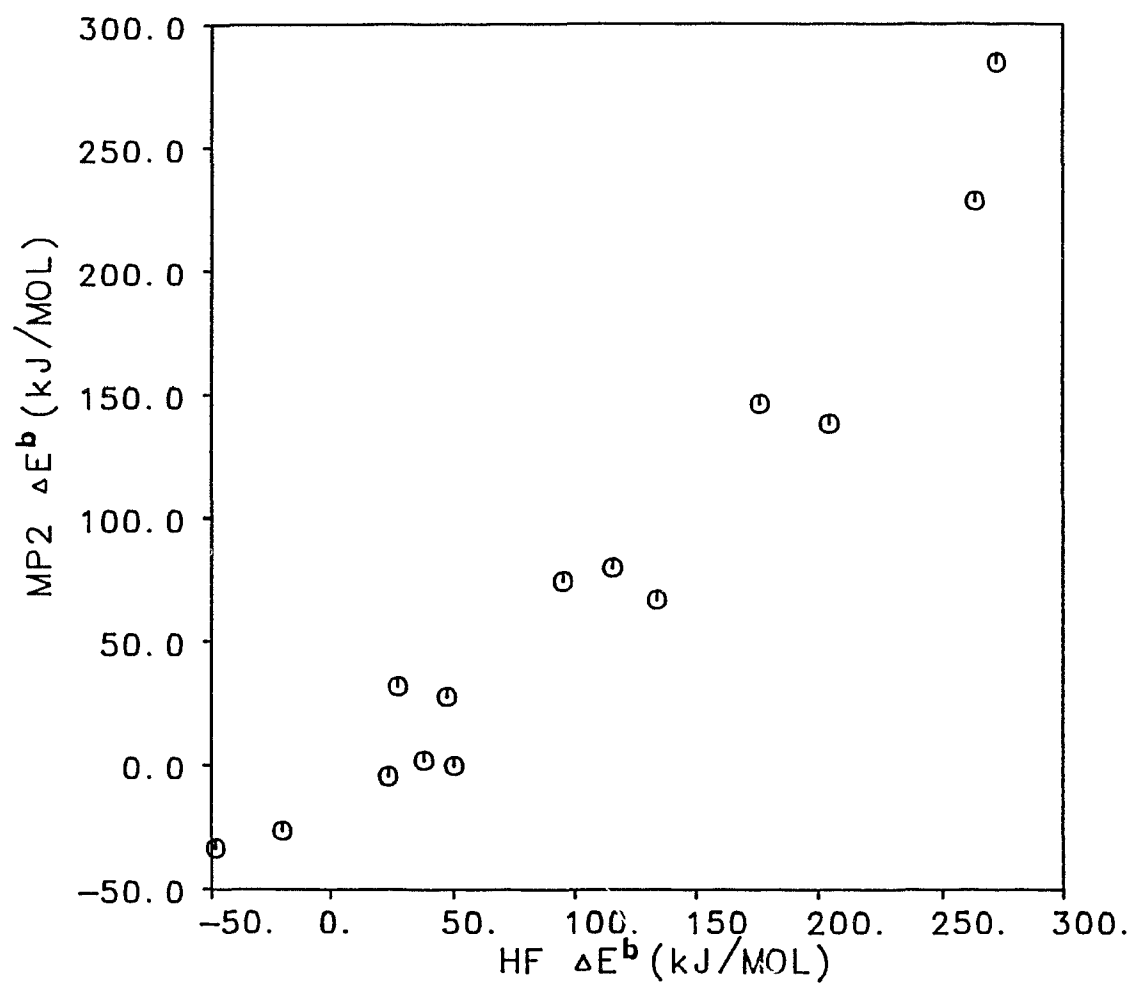


Figure 3.6.8 Comparison of ΔE^b obtained at the HF and MP2 levels.

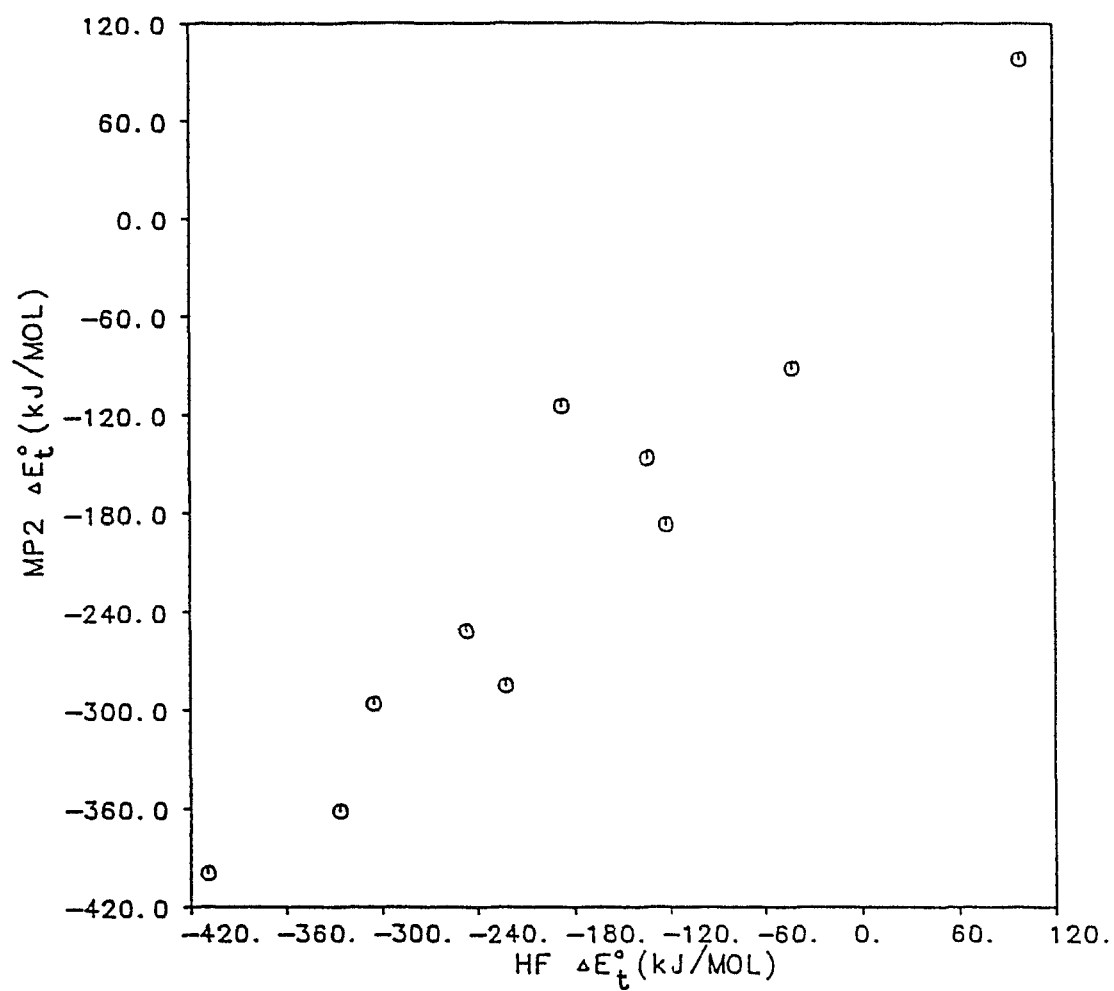


Figure 3.6.9 Comparison of ΔE_t° obtained at the HF and MP2 levels.

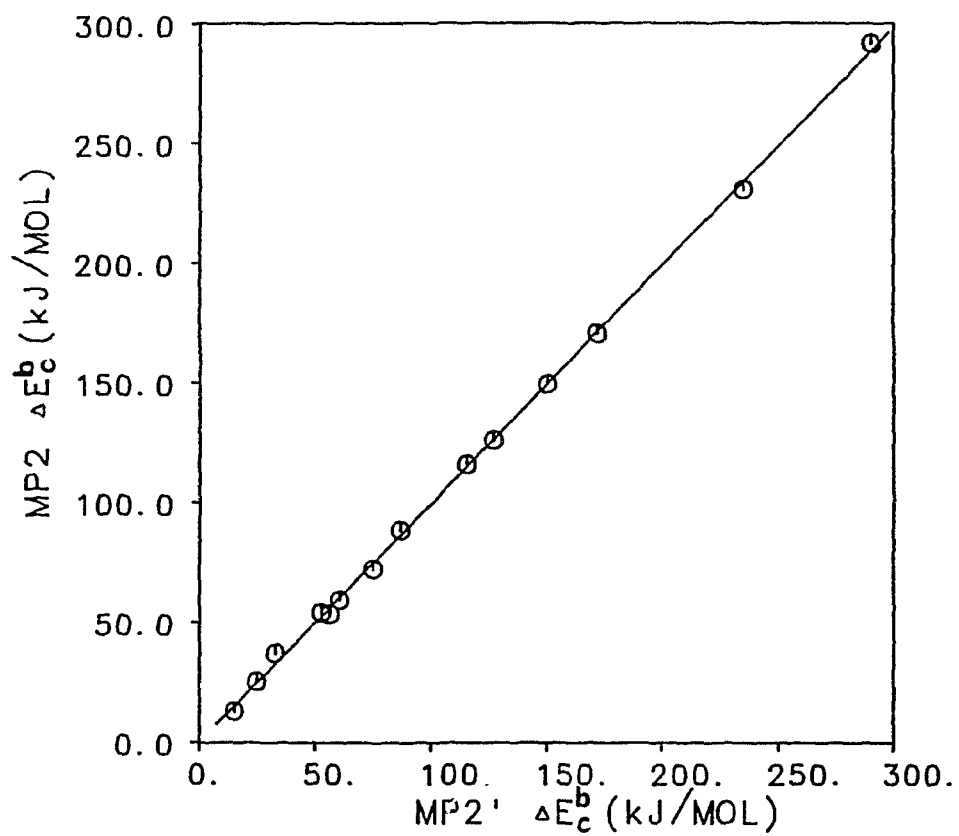


Figure 3.6.10 Comparison of ΔE_c^b obtained at the MP2' and MP2 levels.

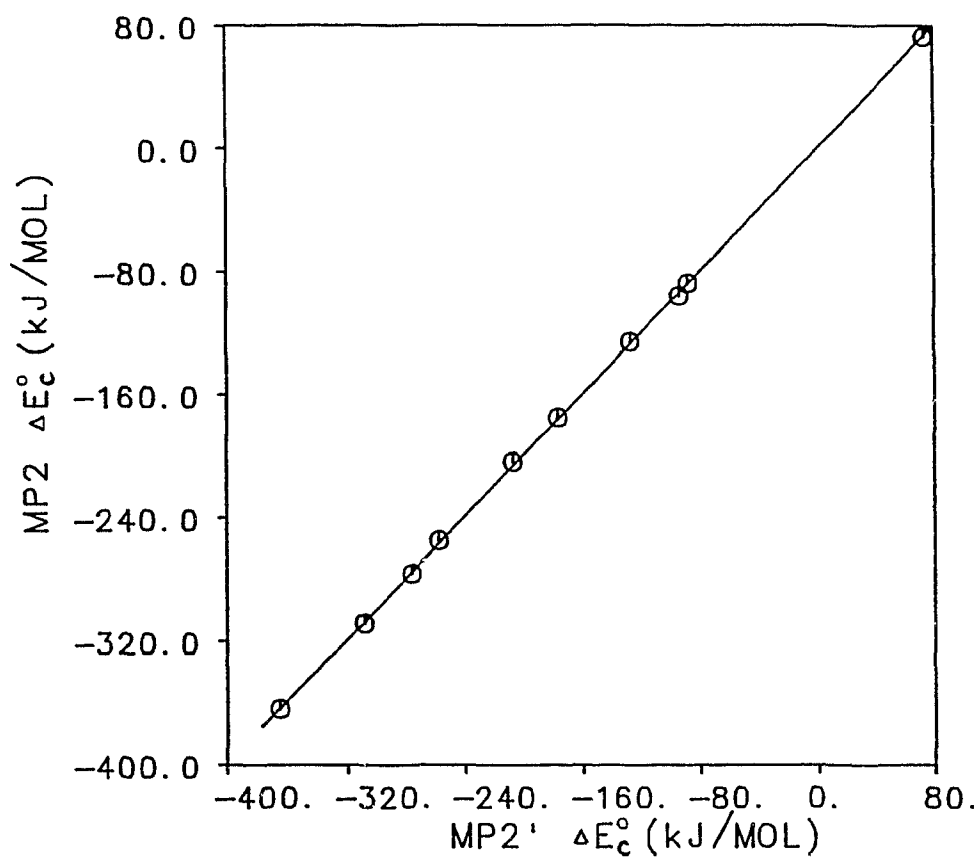


Figure 3.6.11 Comparison of ΔE_c^0 obtained at the MP2' and MP2 levels.

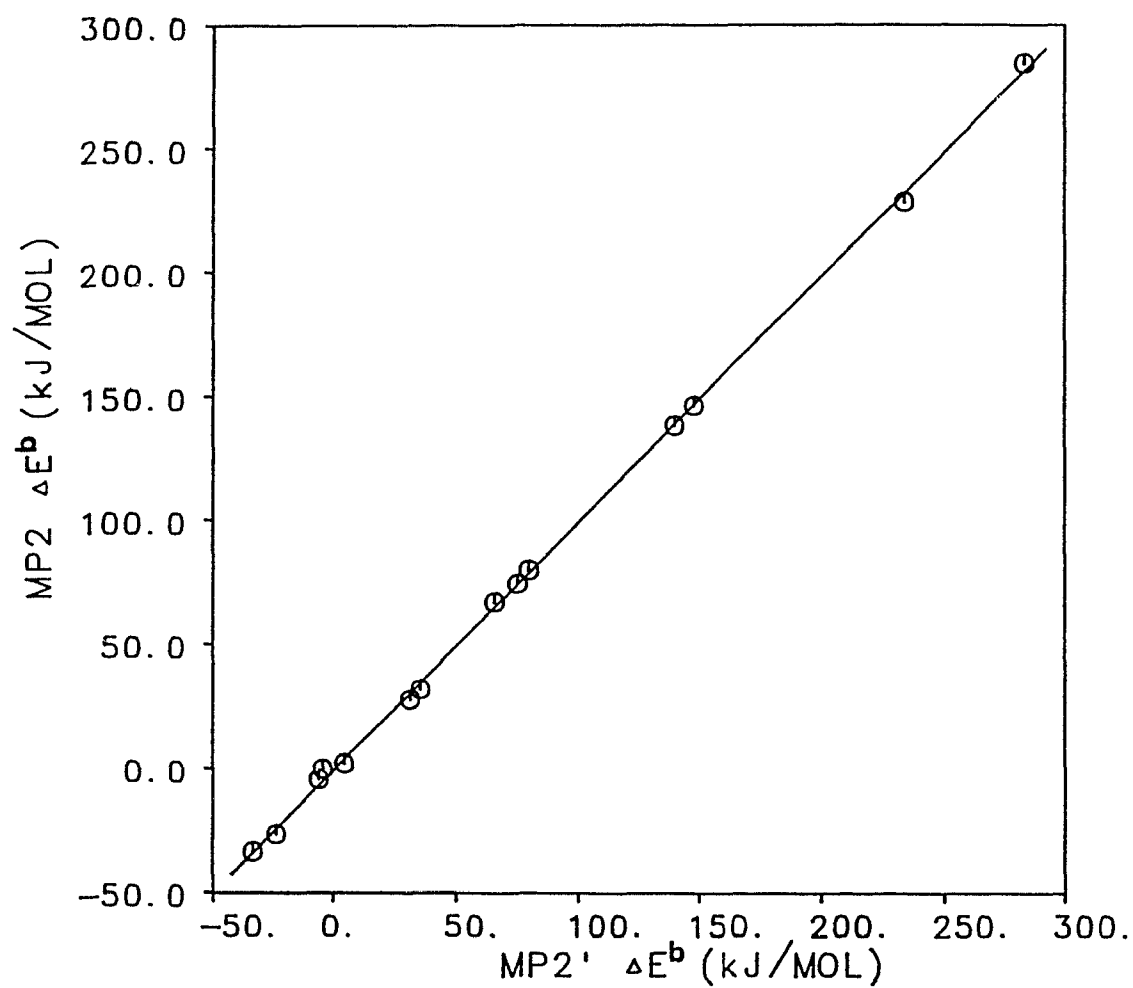


Figure 3.6.12 Comparison of ΔE^b obtained by the MP2' and MP2 methods.

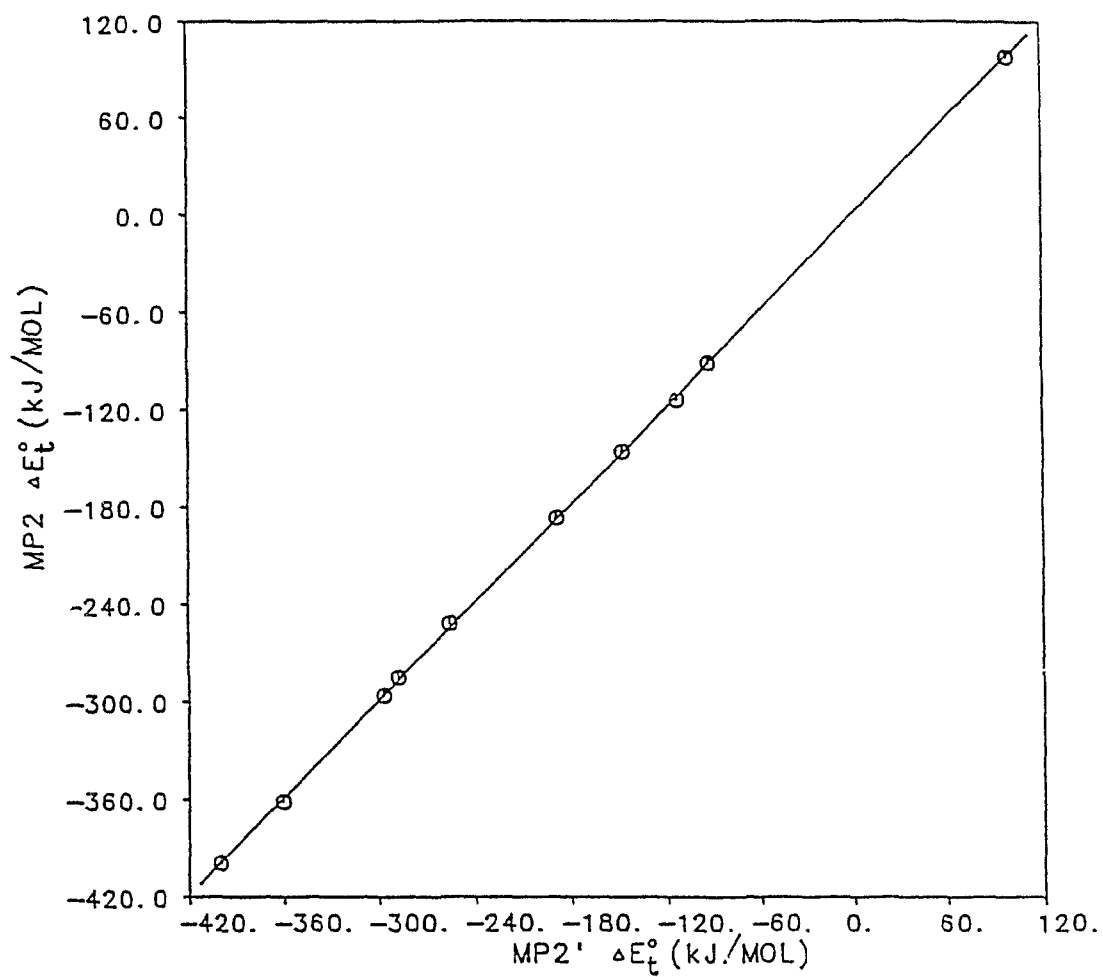


Figure 3.6.13 Comparison of ΔE_t° calculated at the MP2' and MP2 levels.

Chapter 4

Intrinsic Barriers of Model S_N2 Reactions

4.1 Overview

The concept of an intrinsic barrier was introduced by Marcus when he developed a theory for electron-transfer reactions.⁵⁵ He proposed an equation (see eq. 4.1.1), in which the free energy of activation is

$$\Delta G^\ddagger = \Delta G^\ddagger_0 + 0.5 \Delta G^\circ + \frac{(\Delta G^\circ)^2}{16\Delta G^\ddagger_0} \quad (4.1.1)$$

related not only to the free energy of a reaction (ΔG°) but also to $\Delta G^\ddagger_0$. Marcus interpreted the new term $\Delta G^\ddagger_0$ as the reorganization energy, i.e., the energy changes necessary to reach the TS by bond lengthening, compression and/or torsion, bond angle changes and reorganization of solvent molecules. According to eq. 4.1.1, $\Delta G^\ddagger_0$ equals $\Delta G^\ddagger$ when ΔG° is zero. That is, $\Delta G^\ddagger_0$ is the activation barrier that would exist in the absence of any thermodynamic driving force. Therefore, it is called the intrinsic barrier and may be thought of as the purely kinetic contribution to the reaction barrier.

The concept of an intrinsic barrier provides a way of thinking and valuable insight into the reaction process. For example, the anomalous values of the Brönsted coefficient ($\alpha > 1$) can be explained by the large variation of the intrinsic barriers within a series of reactions.^{55c} Also the breakdown of the rate-equilibrium relationship and the reactivity-selectivity principle can be explained in terms of the

variation of the intrinsic barriers.^{31d}

The Marcus equation has been successfully used in a wide range of reactions. In the application of the Marcus equation to the deprotonation of carbon acids, Bunting and Stefanidis⁵⁶ found that the $\Delta G^\ddagger$ calculated from eq. 4.1.1 vary systematically with the energies of reactions. Since $\Delta G^\ddagger$ is linear in ΔG° within each series of ketones, they suggested a two-parameter modification of the simple Marcus relationship, in which $\Delta G^\ddagger$ is replaced by eq. 4.1.2

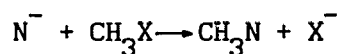
$$\Delta G^\ddagger = A + B \Delta G^\circ \quad (4.1.2)$$

In this expression, A is interpreted as the "true" intrinsic barrier at $\Delta G^\circ = 0$ and the parameter B is the main reflection of imbalances between those factors (resonance, solvation, etc.). And they indicate that B values should be the largest in those systems in which Bernasconi's principle of nonperfect synchronization is most important.^{56a}

The Marcus relationship has been used also in the study of methyl transfer (S_N2) reactions.⁵⁷ The S_N2 reaction is one of the most widely studied families of reactions in chemistry. Investigations of S_N2 reactions have played an important role in the development of fundamental ideas in physical organic chemistry, such as structure-reactivity relationships, linear free energy relationships, steric inhibition, kinetics as a probe of mechanism, stereochemistry as a probe of mechanism, and solvent effects. Nevertheless, there are still some fundamental problems with the S_N2 reactions. In fact, it is still not possible to predict the reactions in simple terms.^{46,58} Attempts

have been made to correlate the intrinsic barriers with thermodynamic properties.^{44,58a,59}

In this chapter, results obtained at the MP2' computational level (unless otherwise indicated) are used to study the intrinsic barriers and reactivities of the following reactions



where N = H, X = H, NH₂, OH, OOH, F, NC, CCH, CN, PH₂, SH and Cl; N = F, X = H, NH₂, OH, F, NC, CCH, CN, PH₂, SH and Cl. The computational details are given in section 3.2. The justification of using the MP2' results is discussed in section 3.6. The intention is to provide a molecular understanding of the factors that determine the height of the intrinsic barrier. Furthermore, the rate-equilibrium relationship and the parameter α are discussed.

4.2 Intrinsic Barriers of Model S_N2 Reactions

Strictly speaking, the Marcus equation is only valid for an elementary reaction. Gas phase S_N2 reactions involve three elementary steps. The second step which involves the conversion of the reactant ion-molecule complex to the product ion-molecule complex is the main step which affects the efficiency of the reaction. Thus, the Marcus equation is used to analyse this elementary step. The potential energy form of the Marcus equation 4.1.1 is^{55a}

$$\Delta E^\ddagger = \Delta E^\ddagger + 0.5 \Delta E^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E^\ddagger} \quad (4.2.1)$$

According to eq. 3.3.4 and 3.3.5, ΔE_c^b is equivalent to $\Delta E^\ddagger$ (energy barrier) and ΔE_c° is equivalent to ΔE° (energy change of the reaction). ΔE° is called an intrinsic barrier as well.

The concept of an intrinsic barrier provides a better understanding of reaction processes. If the intrinsic barriers are equal for a series of reactions, then the different reactivities are a direct result of different thermodynamic driving forces. In this case, the Brönsted equation is equivalent to the Marcus equation. However, if the intrinsic barriers are not equal, the reactivities can not be explained merely by the thermodynamic properties. The reason why the linear relationship only exists for a series of reactions is explained by the intrinsic barrier. The intrinsic barrier for a symmetric reaction can be understood intuitively. For asymmetric reactions, however, it is not obvious. Nevertheless, by making some approximations, the meaning of the intrinsic barrier can be revealed. If the activation energy for the forward reaction is denoted as $\Delta E_f^\ddagger$ and that for the reverse reaction is denoted as $\Delta E_r^\ddagger$, then by omitting the quadratic term (which is usually small⁶⁰) in eq. 4.2.1, we have

$$\Delta E_f^\ddagger + \Delta E_r^\ddagger = 2 \Delta E^\circ + \frac{(\Delta E^\circ)^2}{8 \Delta E^\circ} \approx 2 \Delta E^\circ \quad (4.2.2)$$

Thus

$$\Delta E^\circ = 0.5 (\Delta E_f^\ddagger + \Delta E_r^\ddagger) \quad (4.2.3)$$

That is, the intrinsic barrier of an asymmetric reaction is the average

activation energy of the forward and reverse reactions.

For asymmetric reactions, $\Delta E^\ddagger$ values can be calculated from eq. 4.2.1 or eq. 4.2.4

$$\Delta E^\ddagger_{(xy)} = 0.5 (\Delta E^\ddagger_{(xx)} + \Delta E^\ddagger_{(yy)}) \quad (4.2.4)$$

where $\Delta E^\ddagger_{(xx)}$ and $\Delta E^\ddagger_{(yy)}$ are intrinsic barriers to symmetric reactions $X^- + RX \rightarrow X^- + RX$ and $Y^- + RY \rightarrow Y^- + RY$, respectively. Table 4.2.1 provides values of $\Delta E^\ddagger$ calculated by means of eq 4.2.1 together with $\Delta E^\ddagger$ and ΔE° values. Clearly, the $\Delta E^\ddagger$ values differ from reaction to reaction. Plots of $\Delta E^\ddagger$ versus ΔE° are shown in Fig. 4.2.1 and 4.2.2 for reactions with the same nucleophile $N = H$ and $N = F$, respectively. It appears that in these plots, the reactions manifest themselves into groups. Within each group, $\Delta E^\ddagger$ is a function of ΔE° . Using the Bunting and Stefanidis two-parameter relationship (eq. 4.1.2) to analyse the data, when $N = H$, the first group with $X = CCH$, $\underline{CN}$ and $\underline{NC}$ has an $A = 269.57(\text{kJ/mol})$ and $B = 0.27$. The second group, $X = PH_2$, SH and Cl , has an $A = 249.86$ and $B = 0.30$. The third group, $X = NH_2$, OH , OOH and F , has an $A = 225.35$ and $B = 0.36$. Whereas when $N = F$, the group $X = CCH$, $\underline{CN}$ and $\underline{NC}$ has an $A = 100.08$ and $B = 0.18$. The group $X = PH_2$, SH and Cl has an $A = 84.96$ and $B = 0.23$. The Group $X = NH_2$, OH and F has an $A = 53.69$ and $B = 0.25$.

Bunting and Stefanidis interpreted A as the "true" intrinsic barrier. However, the A value for a reaction can be different depending on the reactions with which it is grouped. For example, for reaction $N^- + CH_3X \rightarrow CH_3N + X^-$, the A value can be obtained by grouping the reactions which have the same N but different X or by grouping the reactions which have

Table 4.2.1 Intrinsic barriers at the MP2' level (kJ/mol).

$N^- + RX$	$\Delta E^\ddagger$	$\Delta E^\ddagger$	ΔE°
$H^- + RCCH$	231.56	172.35	-127.13
$H^- + RCN$	218.34	127.25	-206.61
$H^- + RNC$	182.45	60.83	-308.41
$H^- + RPH_2$	190.20	108.07	-187.31
$H^- + RSH$	173.73	56.50	-275.74
$H^- + RCl$	136.97	15.35	-364.49
$H^- + RNH_2$	191.90	150.45	-87.92
$H^- + ROH$	163.51	87.14	-176.57
$H^- + ROOH$	152.95	68.03	-203.77
$H^- + RF$	129.72	32.93	-257.47
$F^- + RCCH$	122.55	200.79	137.26
$F^- + RCN$	117.52	153.94	67.92
$F^- + RNC$	92.00	76.26	-32.97
$F^- + RPH_2$	103.12	147.14	80.23
$F^- + RSH$	83.60	79.79	-7.70
$F^- + RCl$	63.31	25.13	-93.71
$F^- + RNH_2$	92.70	188.95	158.58
$F^- + ROH$	74.18	115.85	74.09

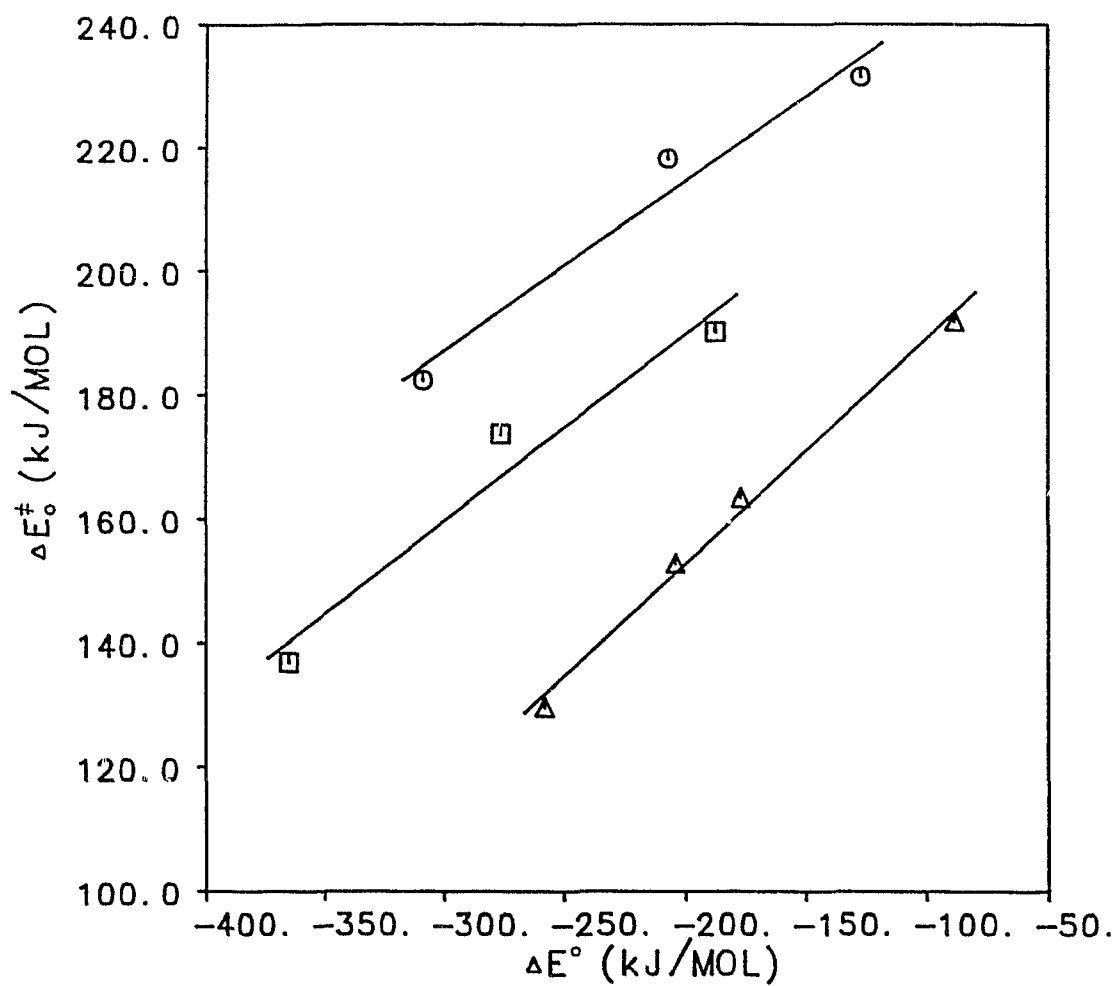


Figure 4.2.1 A plot of $\Delta E^\ddagger$ versus ΔE° for reactions $\text{H}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_4 + \text{X}^-$.

Data set (O), X = CCH, CN and NC;

data set (□), X = PH_2 , SH and Cl;

and data set (Δ), X = NH_2 , OH, OOH and F.

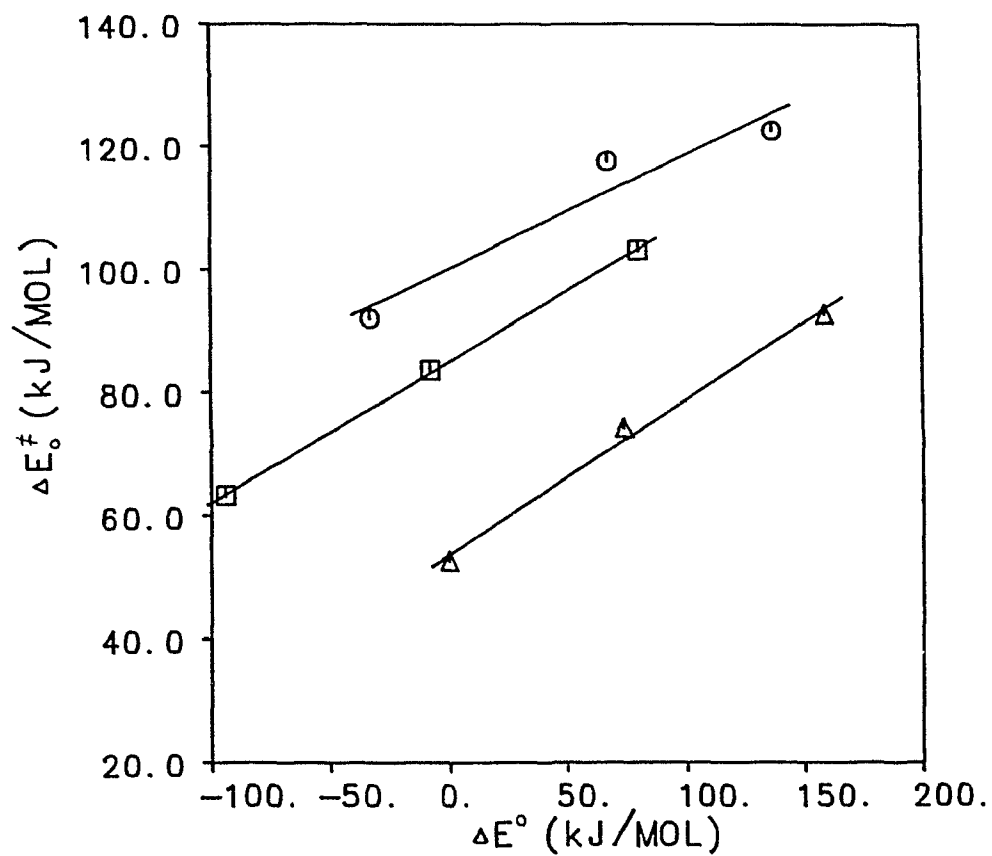


Figure 4.2.2 A plot of $\Delta E^\ddagger$ versus ΔE° for reactions $F^- + CH_3X \rightarrow CH_3F + X^-$.

Data set (O), $X = CCH, \underline{CN}$ and $\underline{NC}$;

data set (□), $X = PH_2, SH$ and Cl ;

and data set (Δ), $X = NH_2, OH$ and F .

the same X but different N. If N and X are not the same, the A value is likely to be different as well. Therefore, A and B are really group properties. Nevertheless, if reactions are correlated by the Bunting and Stefanidis equation, the rate-equilibrium relationship is observed. This will be discussed further in the next section. Thus, the Bunting and Stefanidis relationship can be used to distinguish different reaction processes. With the same nucleophile, X = CCH, $\underline{\text{CN}}$ and $\underline{\text{NC}}$ are related by the Bunting-Stefanidis equation and they are said to belong to the first group. X = PH_2 , SH and Cl is the second group, and X = NH_2 , OH, OOH and F is the third group. The different behaviour of CCH, $\underline{\text{CN}}$ and $\underline{\text{NC}}$ is observed in experiments as well. Brauman *et al.* explained this difference by hybridized orbitals.^{44,61} The concept of hybridized orbitals provides a simple picture of bonding. If an atom uses its *sp* hybridized orbital to form a bond, it usually uses the two perpendicular *p* orbitals to form π bonds at the same time. For a CH_3X molecule in which the X group is *sp* hybridized, the X group can not form a triple bond with the central carbon, but some kind of delocalization or hyperconjugation may exist. Here, CCH, $\underline{\text{CN}}$ and $\underline{\text{NC}}$ have *sp* hybridized orbitals whereas the other groups have sp^3 hybridized orbitals. Hydrogen is a special case, since it only has one occupied *s* orbital, and it is expected to behave differently. The differences between the second and the third group can be explained in terms of their electronic structures in the TS which in turn are a result of differences in electronegativities and polarizabilities. The second group needs ψ_3 (corresponding to the configuration $\text{N}^- \text{R}^+ \text{X}^-$) to reach the TS while the third group does not need the ψ_3 configuration (see Table 3.4.4).

Actually, the first group is a combination of two groups which have different electronic structures in the TS, i.e. one group contains CCH and $\underline{\text{CN}}$ and while the other group contains only $\text{X} = \underline{\text{NC}}$. It would be desirable to include more X which have the same properties as $\underline{\text{NC}}$, i.e. *sp* hybridized and large electronegativity. However, it is difficult to identify such groups which are computationally manageable.

The different behaviours of these groups also manifest themselves in Fig. 4.2.3 and Fig. 4.2.4 where the plots are obtained by the following procedure. Firstly, for the reactions with the same nucleophile the position of the product is assigned a reaction coordinate equal to unity (point a in Fig. 4.2.3) and its energy is taken to be zero. Secondly, assuming that the energy profile of the product configuration is not a function of the leaving group (X), for different X the product energy profile can be approximated by the same straight line (line ab). This is justified by the fact that the properties of N affect the shape of the product energy profile more than those of X. Thirdly, using the ΔE° value for the reaction $\text{N}^- \cdots \text{CH}_3\text{X} \rightarrow \text{CH}_3\text{N}^- \cdots \text{X}^-$, the relative position of the reactant is located at a reaction coordinate equal to zero (point c). Fourthly, using the assumption that the TS occurs at the intersection point of the reactant and product energy profiles, the TS must lie on line ab and using the value of $\Delta E^\ddagger$, the TS is located (point d). And finally, by connecting points c and d, the reactant energy profile is obtained. Fig. 4.2.3 and 4.2.4 show that for those X's (first group) which are *sp* hybridized and have large A in Fig. 4.2.1 and 4.2.2, their reactant energy profiles exhibit a rapid ascent of the potential energy as a function of reaction coordinate. For those X's (third group)

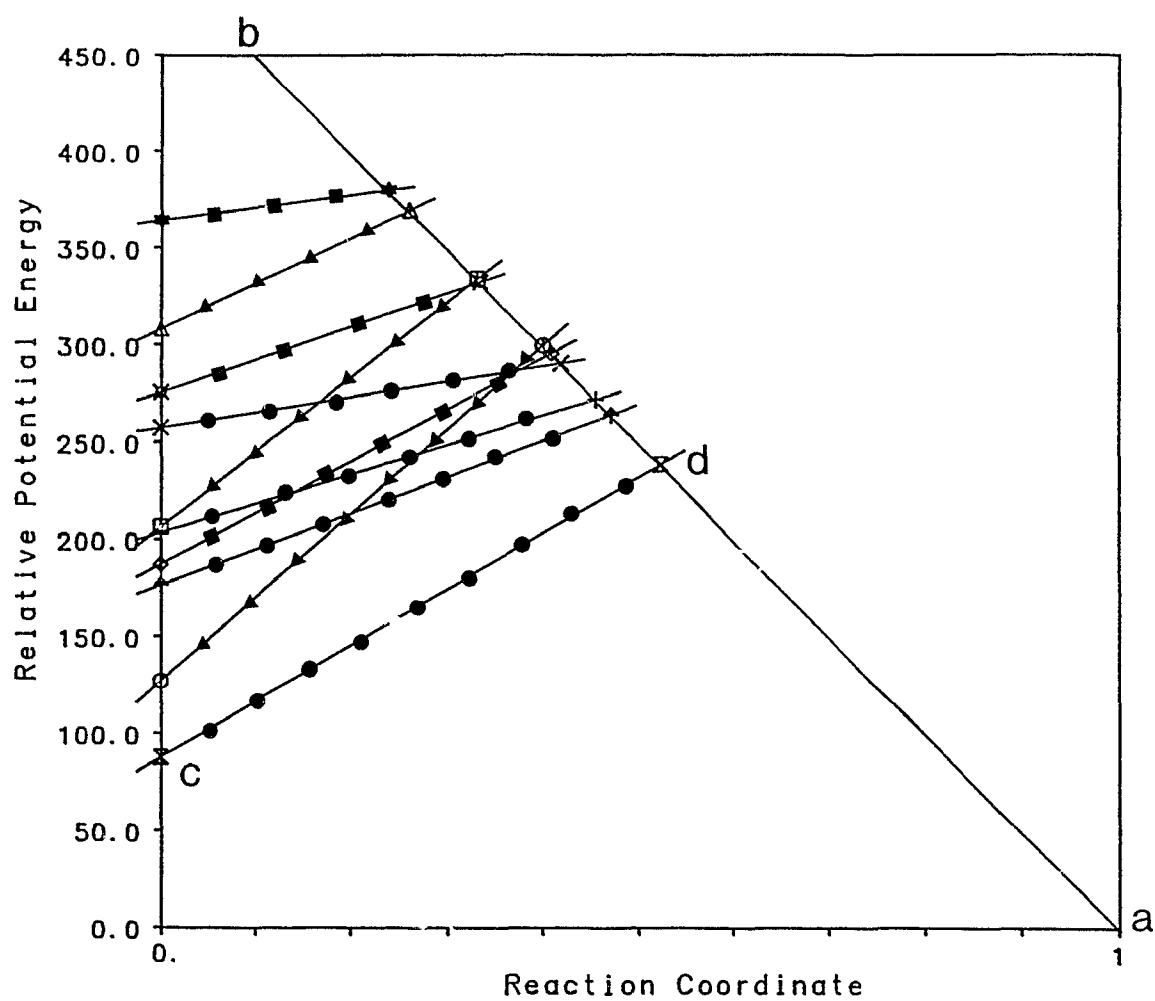


Figure 4.2.3 Reaction profiles for the reactions $\text{H}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_4 + \text{X}^-$.

Legend: $\text{X} = \text{CCH}, \underline{\text{CN}}$ and $\underline{\text{NC}}$ ($\triangleleft \triangleleft$);

$\text{X} = \text{PH}_2, \text{SH}$ and Cl ($\blacksquare \blacksquare$);

and $\text{X} = \text{NH}_2, \text{OH}, \text{OOH}$ and F ($\bullet \bullet$).

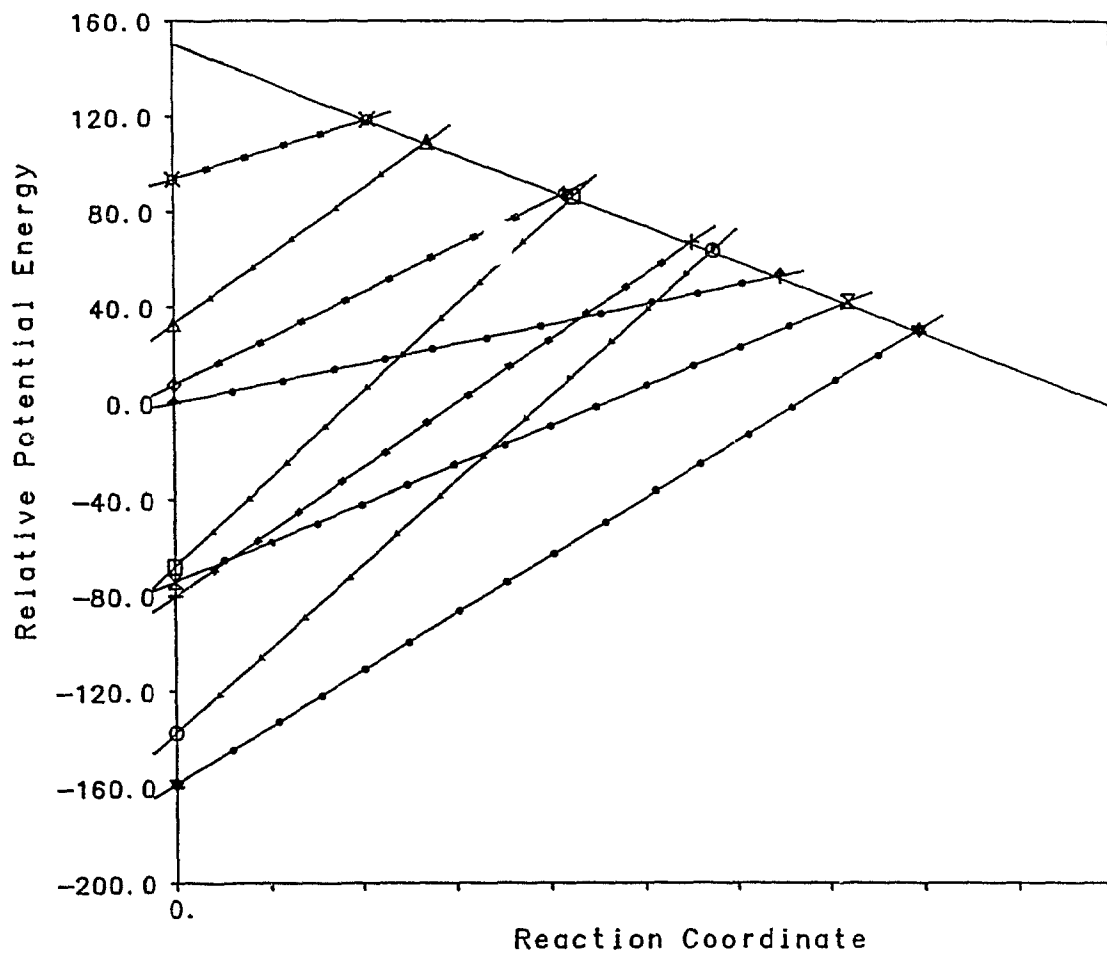


Figure 4.2.4 Reaction profiles for the reactions $\text{F}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_3\text{F} + \text{X}^-$.

Legend: X = CCH, CN and NC ($\leftarrow \leftarrow \leftarrow$);

X = PH_2 , SH and Cl ($\blacksquare \blacksquare \blacksquare$);

and X = NH_2 , OH and F ($\bullet \bullet \bullet$).

which have small A in Fig. 4.2.1 and 4.2.2, the energy profiles exhibit a slow ascent of the potential energy as a function of the reaction coordinate.

For the symmetric reactions, $\Delta E^\ddagger = \Delta E^\ddagger = A$. Thus, the value of A is not a group property and it is the "true" intrinsic barrier. The intrinsic barrier of the symmetric reaction is a very important property. If the intrinsic barriers of the symmetric reactions are known, the $\Delta E^\ddagger$ values of asymmetric reactions can be obtained immediately from eq. 4.2.4. Moreover the activation energy $\Delta E^\ddagger$ can be calculated easily from eq. 4.2.1. Table 4.2.2 lists the calculated $\Delta E^\ddagger$ values for symmetric reactions together with the topological G values, which are defined by

$$G = \rho r_c \quad (4.2.5)$$

where ρ is the electron density at the position of the C-X bond critical point in molecule CH_3X and r_c is the distance between carbon and the bond critical point. Studies³ have shown that the ρ value at the critical point provides information about the type of bond involved, whereas the distance r_c provides information about relative electronegativities of the bonded atoms as mentioned in section 3.5. The large ρ and r_c values mean that the relative electronegativity of carbon is large. Thus, a large G value indicates that the electronegativity of X is relatively small. Data in Table 4.2.2 indicate that the $\Delta E^\ddagger$ values of symmetric reactions are related to G values within each group of reactions. To predict the intrinsic barrier of symmetric reactions, the

Table 4.2.2 Calculated G values for RX and intrinsic barriers of
 symmetric reactions $X^- + RX \rightarrow X^- + RX$ (a.u.).

RX	$\Delta E^\ddagger_a$	G
RH	0.08956	0.364
RCCH	0.08683	0.341
RCN	0.07676	0.328
RNC	0.04942	0.234
RPH ₂	0.05533	0.327
RSH	0.04278	0.296
RCI	0.01478	0.267
RNH ₂	0.05662	0.305
ROH	0.03499	0.245
ROOH	0.02695	0.238
RF	0.00925	0.216

^a Intrinsic barriers $\Delta E^\ddagger_{(HX)}$ calculated by use of eq. 4.2.1 first and then combined with $\Delta E^\ddagger_{(HH)}$ to calculate $\Delta E^\ddagger_{(XX)}$ by use of eq. 4.2.4.

following equation is proposed

$$\Delta E^\ddagger = 0.8275G - G' \quad (4.2.6)$$

The G' value varies from one group to another. The groups are classified according to the type of hybridization and the electronic structure of the transition state. Thus, for group I ($X = \text{CCH}$ and $\underline{\text{CN}}$) $G' = 0.1963$; for group II ($X = \underline{\text{NC}}$), $G' = 0.1444$; for group III ($X = \text{PH}_2$, SH and Cl), $G' = 0.2075$, and for group IV ($X = \text{NH}_2$, OH , OOH and F), $G' = 0.1696$. The $\Delta E^\ddagger$ values calculated by use of eq. 4.2.6 are compared with the values calculated by use of eq. 4.2.4 in Fig. 4.2.5. Except for NH_2 , the correlation is generally good. Thus, as long as the ground state G value is available, it is possible to predict the $\Delta E^\ddagger$ value. For example, G values for CH_2Cl_2 , CHCl_3 and CCl_4 are 0.278, 0.296 and 0.309, respectively at the HF calculation level while at the same level the G value for CH_3Cl is 0.254. Since they all belong to group III, their $\Delta E^\ddagger$ values increase as the G value increases. This prediction is consistent with that of Shaik and Pross.^{31d,62} The present analysis may be compared with that of Shaik and Pross, in which they use a curvature factor f and an energy gap factor ($I_{\text{N:}} - A_{\text{RX}}$) to explain the intrinsic barrier. The f factor is proportional to $W_{\text{R:}}$ which accounts for the delocalization properties of the charge-transfer states. The f factor appears to be equivalent to the hybridization factor discussed above. However, the results are not all the same. According to their calculation: CCH and OH have similar f factors ($W_{\text{R:}} = 0.36$); F and Cl have similar f factors ($W_{\text{R:}} \sim 0.24 - 0.25$); and $W_{\text{R:}} = 0.30$ for $\underline{\text{CN}}$. According to their model,

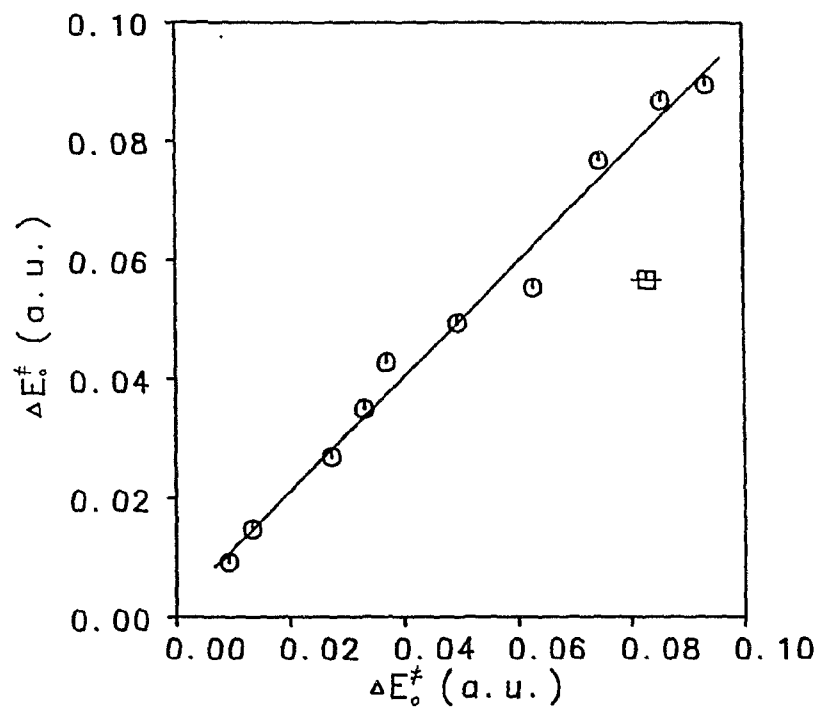


Figure 4.2.5 A plot of $\Delta E^\ddagger$ obtained from eq. 4.2.6 (horizontal axis) versus $\Delta E_0^\ddagger$ obtained from eq. 4.2.4 (vertical axis). The data point for $X \approx \text{NH}_2$ (denoted by $\square$) is excluded from the best fit line.

the $\Delta E^\ddagger$ value for the symmetric reaction $N = X = F$ is larger than that of the reaction $N = X = Cl$, since the energy gap ($I_{N:} - A_{RX}$) is larger for the reaction $N = X = F$. This prediction is consistent with the HF results reported in this thesis (Table 3.3.1) and HF calculations in the literature.⁶³ The experimental result for reaction $N = X = Cl$ is available, but not for $N = X = F$. Brauman *et al.* predicted that $N = X = Cl$ has a lower intrinsic barrier.⁴⁴ In this work, results obtained at the MP2' and MP2 levels show that $N = X = F$ has a lower intrinsic barrier. It would be interesting to see the results of calculations at even higher levels.

It is also noted that within each group, the intrinsic barrier $\Delta E^\ddagger$ of a symmetric reaction is related to the charge (Q_X) on X in molecule CH_3X , (see Table 4.2.3). As discussed above, the $\Delta E^\ddagger$ value is related to the electronegativity of X within each group. Since Q_X is a measure of the electronegativity of X, the relationship between $\Delta E^\ddagger$ and Q_X is not unexpected. Furthermore, it is noted that within each group the intrinsic barrier is related to the base strength of X^- (pK_a), see Table 4.2.4. As the base strength increases (pK_a increases), the intrinsic barrier increases. This can be understood by the fact that the base strength of X^- reflects the electron loosing ability of X^- . And it is an indication of the electronegativity of X as well.

In summary, the intrinsic barrier is a reorganization energy. For a symmetric S_N2 reaction, it is mainly related to the type of bonding between carbon and the leaving group (or entering nucleophile). The reactions can be classified according to the hybridization of X, specifically, the atom adjacent to carbon, and the electronic structure

Table 4.2.3 Charge on X in molecule RX.

RX	$\Delta E^\circ{}^a$ (kJ/mol)	$-Q_X(e)$
RH	235.15	-0.066
RCCH	227.97	0.290
RCN	201.52	0.328
RNC	129.76	0.650
RPH ₂	145.26	-0.515
RSH	112.31	-0.003
RCI	38.80	0.224
RNH ₂	148.64	0.350
ROH	91.87	0.545
ROOH	70.75	0.604
RF	24.30	0.626

^a See footnote a in Table 4.2.2.

Table 4.2.4 Basicity of X^- in gas phase and in solution.

RX	$\Delta E^\circ{}^a$ (kJ/mol)	pK_a^b	ΔH^c (kJ/mol)
RH	235.15	35	1676
RCCH	227.97	24	1572
<u>RCN</u>	201.52	9.21	1478
<u>RNC</u>	129.76		
RPH ₂	145.26	29	1551
RSH	112.31	7.0	1480
RCI	38.80	-6 to -7	1395
RNH ₂	148.64	32.5	1673
ROH	91.87	15.7	1636
RCOOH	70.75	11.6 ^d	
RF	24.30	3.18	1555

^a See footnote a in Table 4.2.2.

^b Data from reference 64a.

^c Data from reference 64b. ΔH is the enthalpy change of the reaction
 $HX \rightarrow H^+ + X^-$ in the gas phase at 298K.

^d Data from reference 64c.

of the TS. A *sp* hybridized atom results in a rapid ascent or a large curvature of the potential energy profile and a high intrinsic barrier. A large contribution of ψ_3 to the TS lowers the intrinsic barrier. Within each group, the intrinsic barrier is related to the electronegativity of the X group. As the electronegativity of the X group increases, the intrinsic barrier is lowered. The interpretation of the A value in the Bunting and Stefanidis equation needs caution. For a symmetric reaction, $A = \Delta E^\ddagger$ is the "true" intrinsic barrier. However, for an asymmetric reaction, the values of A and B are clearly group properties.

4.3 The Rate-Equilibrium Relationship and α Values

Due to the rapid development of computer technology and gradient techniques in electronic structure calculations, the transition states of relatively simple reactions can be determined by means of theoretical calculations. Nonetheless for the visualization of the reaction process, there is still a need for simple relationships and simple pictures. In the past, many attempts have been made to correlate reactivity with structural or thermodynamic properties. The first linear relationship was proposed by Brønsted and Pedersen in 1924⁶⁵ when they studied the decomposition of nitramide by base catalysis. They found that the rate of the reaction (*k*) is related to the base strength of the catalyst (*K*) by eq. 4.3.1

$$\log k = \alpha \log K + c \quad (4.3.1)$$

Eq. 4.3.1 is often written in its free energy form

$$\Delta G^\ddagger = \alpha \Delta G^\circ + C \quad (4.3.2)$$

or

$$\delta (\Delta G^\ddagger) = \alpha \delta (\Delta G^\circ) \quad (4.3.3)$$

A molecular interpretation of eq. 4.3.3 was first given by Horiuti and Polanyi in 1935.⁶⁶ They proposed that the energy of the TS corresponds to the intersection of the potential energy curves representing the forming bond and the breaking bond. The parameter α is defined as

$$\alpha = \frac{s_1}{s_1 + s_2} \quad (4.3.4)$$

where s_1 and s_2 are the slopes of the two curves at their point of intersection. Leffler^{29a} gave a physical interpretation of the α value. By assuming the TS properties are intermediate between reactants and products, the α value is interpreted as a parameter that measures the degree of resemblance of the transition state to the products, as compared to its resemblance to the reactants. A more quantitative relationship was given by Marcus⁵⁵

$$\Delta G^\ddagger = \Delta G^\ddagger + 0.5 \Delta G^\circ + \frac{(\Delta G^\circ)^2}{16\Delta G^\ddagger} \quad (4.1.1)$$

or in the potential energy form^{55a}

$$\Delta E^\ddagger = \Delta E^\ddagger_0 + 0.5 \Delta E^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E^\ddagger_0} \quad (4.2.1)$$

According to the Marcus equation α is defined as^{55c}

$$\alpha = 0.5 (1+x) \quad (4.3.5)$$

if $\Delta E^\ddagger_0$ is a constant. Otherwise

$$\alpha = 0.5 (1+x) + (1-x^2) \alpha' \quad (4.3.6)$$

where $x = \frac{\Delta E^\circ}{4\Delta E^\ddagger_0}$ and $\alpha' = \frac{\delta \Delta E^\ddagger_0}{\delta \Delta E^\circ}$. If $\Delta E^\ddagger_0$ is a constant, from eq. 4.2.1 $\Delta E^\ddagger$

and ΔE° can be considered to be linearly related in a small segment.⁶⁷

The Marcus equation reduces to the Brönsted equation. However, for a series of reactions, $\Delta E^\ddagger_0$ is usually not a constant. Thus, the requirement for a linear relationship to exist is that $\Delta E^\ddagger_0$ and ΔE° are linearly related to each other. The Bunting and Stefanidis equation is actually the basic requirement for the existence of a linear relationship and the B value in the Bunting and Stefanidis equation is actually the α' value in the Marcus equation 4.3.6. Plots of $\Delta E^\ddagger$ versus ΔE° for N = H and N = F are shown in Fig. 4.3.1 and 4.3.2. For those reactions which are related by the Bunting and Stefanidis equation, $\Delta E^\ddagger$ is related to ΔE° .

The Leffler interpretation of α , according to which α is considered to be an index of the position of the TS along the reaction coordinate, is widely used in organic chemistry. However, there has been some debate about the validity of using α as a measure of the position of the TS

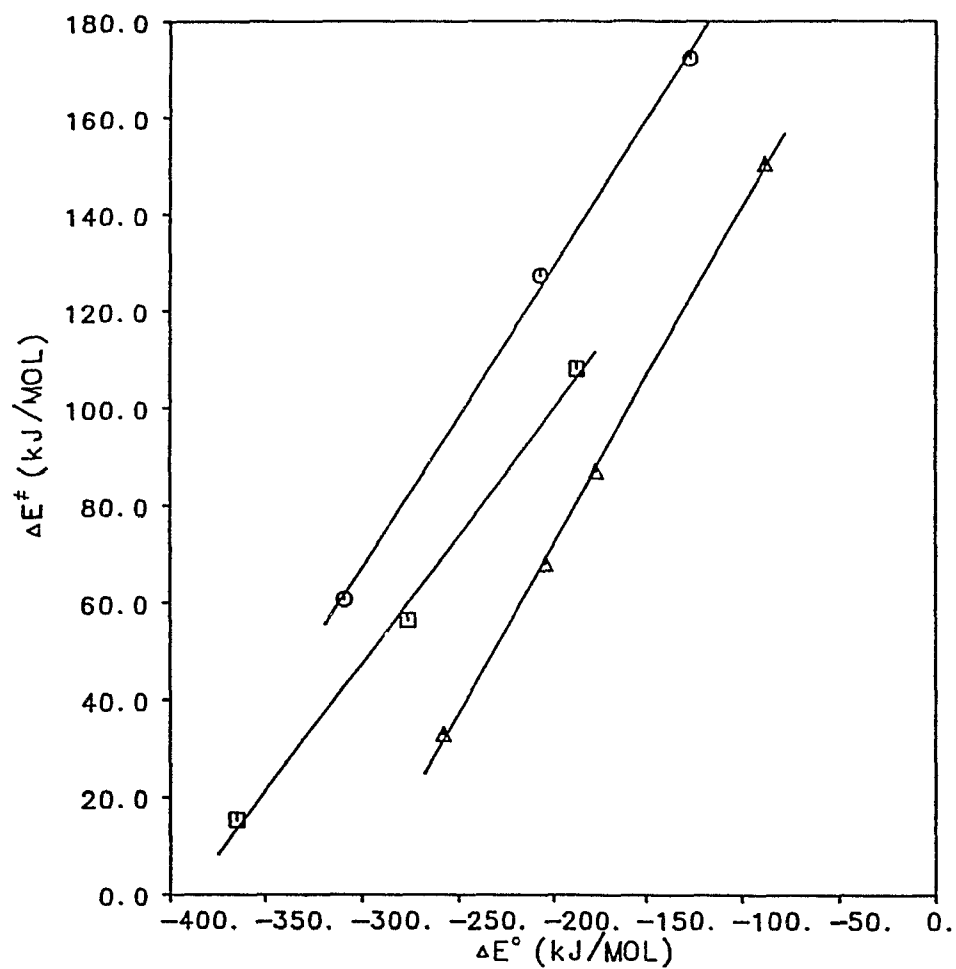


Figure 4.3.1 Plot of $\Delta E^\ddagger$ versus ΔE° for the reactions $\text{H}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_4 + \text{X}^-$.

Legend: X = CCH, CN and NC (O);

X = PH_2 , SH and Cl ($\square$);

X = NH_2 , OH, OOH and F (Δ).

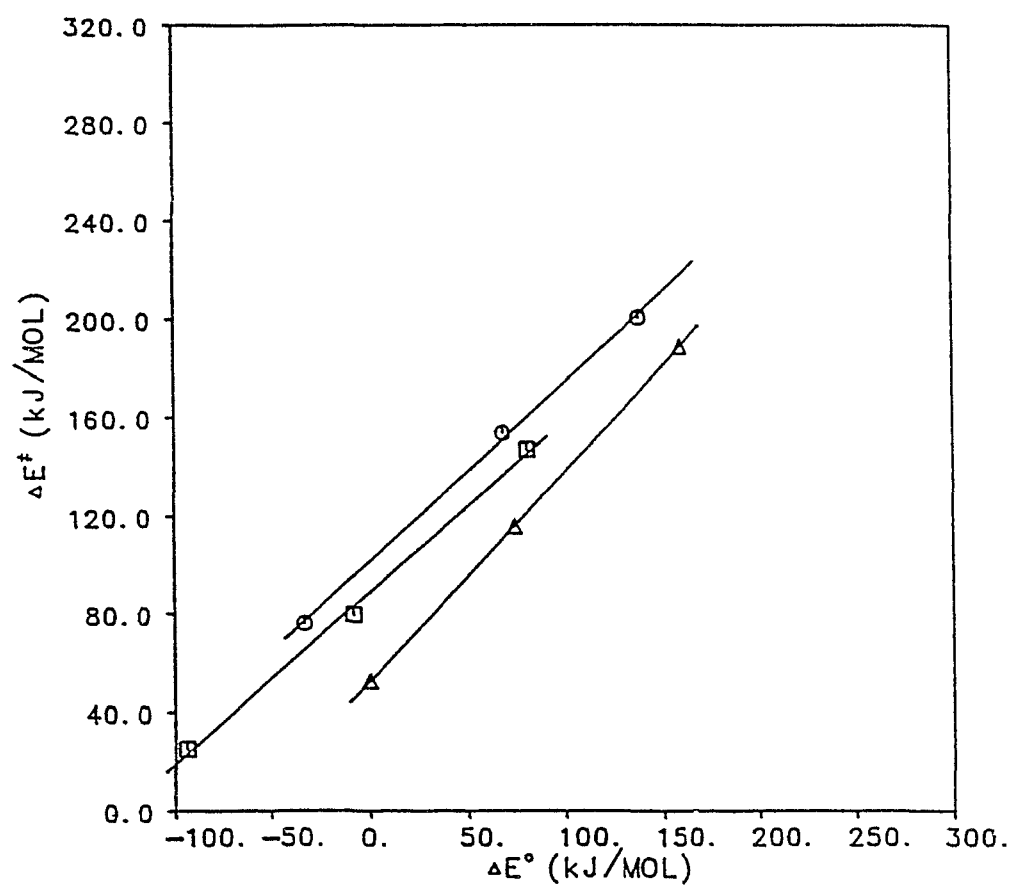


Figure 4.3.2 Plot of $\Delta E^\ddagger$ versus ΔE° for the reactions $F^- + CH_3X \rightarrow CH_3F + X^-$.

Legend: X = CCH, CN and NC (○);

X = PH₂, SH and Cl (□);

X = NH₂, OH and F (Δ).

structure.⁶⁸ Before discussing α further, it is important to clarify which α is discussed in this thesis. Marcus indicated^{55c} that only the α calculated from eq. 4.3.5 can be used as a TS index and it has a normal range of between zero and one. The α obtained from eq. 4.3.6 or the linear plot can not be used as an index of the TS, since the α value so obtained is no longer a property of the reaction. It is a group property as discussed in the previous section. Nevertheless, if the B value (i.e. the α' value in eq. 4.3.6) of the Bunting and Stefanidis equation is small, the α value so obtained can be considered to be an index of the TS, since it does not change much from one reaction to another. By definition, α is an energy index. This is further demonstrated below. The activation energies for the forward and reverse reactions can be expressed using the Marcus equation (eq. 4.2.1). Thus,

$$\begin{aligned} \frac{\Delta E_f^\ddagger}{\Delta E_f^\ddagger + \Delta E_r^\ddagger} &= \frac{\Delta E^\circ + 0.5\Delta E_f^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E^\circ}}{\Delta E^\circ + 0.5\Delta E_f^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E^\circ} + \Delta E^\circ + 0.5\Delta E_r^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E^\circ}} \quad (4.3.7) \\ &= 0.5 + 0.25 \frac{\Delta E^\circ}{\Delta E^\circ + \frac{(\Delta E^\circ)^2}{16\Delta E^\circ}} \end{aligned}$$

and by omitting the quadratic term

$$\frac{\Delta E_f^\ddagger}{\Delta E_f^\ddagger + \Delta E_r^\ddagger} \approx 0.5 + 0.25 \frac{\Delta E^\circ}{\Delta E^\circ}$$

Thus,

$$\alpha \approx 0.5 \frac{\Delta E_f^\ddagger}{\Delta E_f^\ddagger + \Delta E_r^\ddagger} + 0.25 \quad (4.3.8)$$

Fig. 4.3.3 compares the α calculated from eq. 4.3.5 with that calculated from eq. 4.3.8. α is an index of the activation energy in the forward direction for the complete forward and reverse reactions. If the forward activation energy is smaller than the reverse activation energy, then the reaction is exothermic and $\alpha < 0.5$. If the forward activation energy is larger than the reverse activation energy, the reaction is endothermic and $\alpha > 0.5$. Fig. 4.3.4 shows the plot of α (obtained from eq. 4.3.5) versus ΔE° . It appears that for those reactions which are related by the Bunting and Stefanidis equation, α is related to ΔE° .

It is not obvious from the definition of α that α can be used as an index of transition state structure change. However, since both α and structure change are related to the energy, it is possible that under certain circumstances a relationship may exist. To measure the geometry change of the TS, parameters f_R and f_P are proposed. f_R and f_P measure the relative geometry change of the TS as compared to the reactant and product, respectively. For a S_N2 reaction, the major cause of the reorganization energy is the C-X and C-N bond stretching energy.⁵⁹ Thus, f_R and f_P are defined as:

$$f_R = \frac{R_{C-X(TS)} - R_{C-X(Ground)}}{R_{C-X(Ground)}} \quad (4.3.9)$$

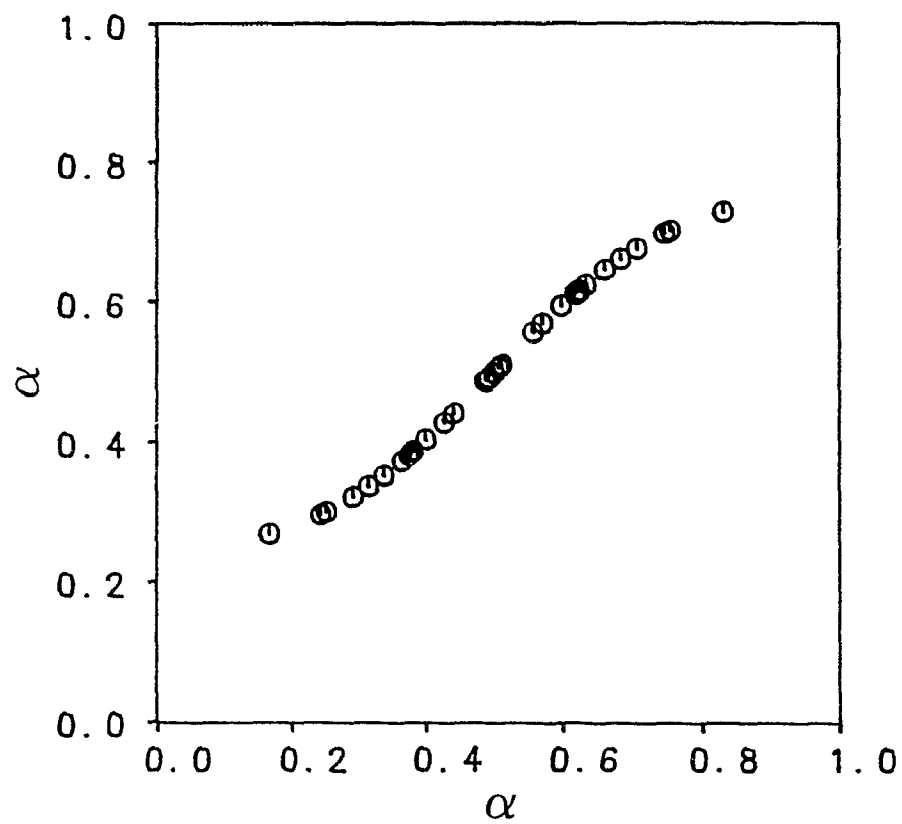


Figure 4.3.3 Comparison of α values calculated from eq. 4.3.5
(horizontal axis) and from eq. 4.3.8 (vertical axis).

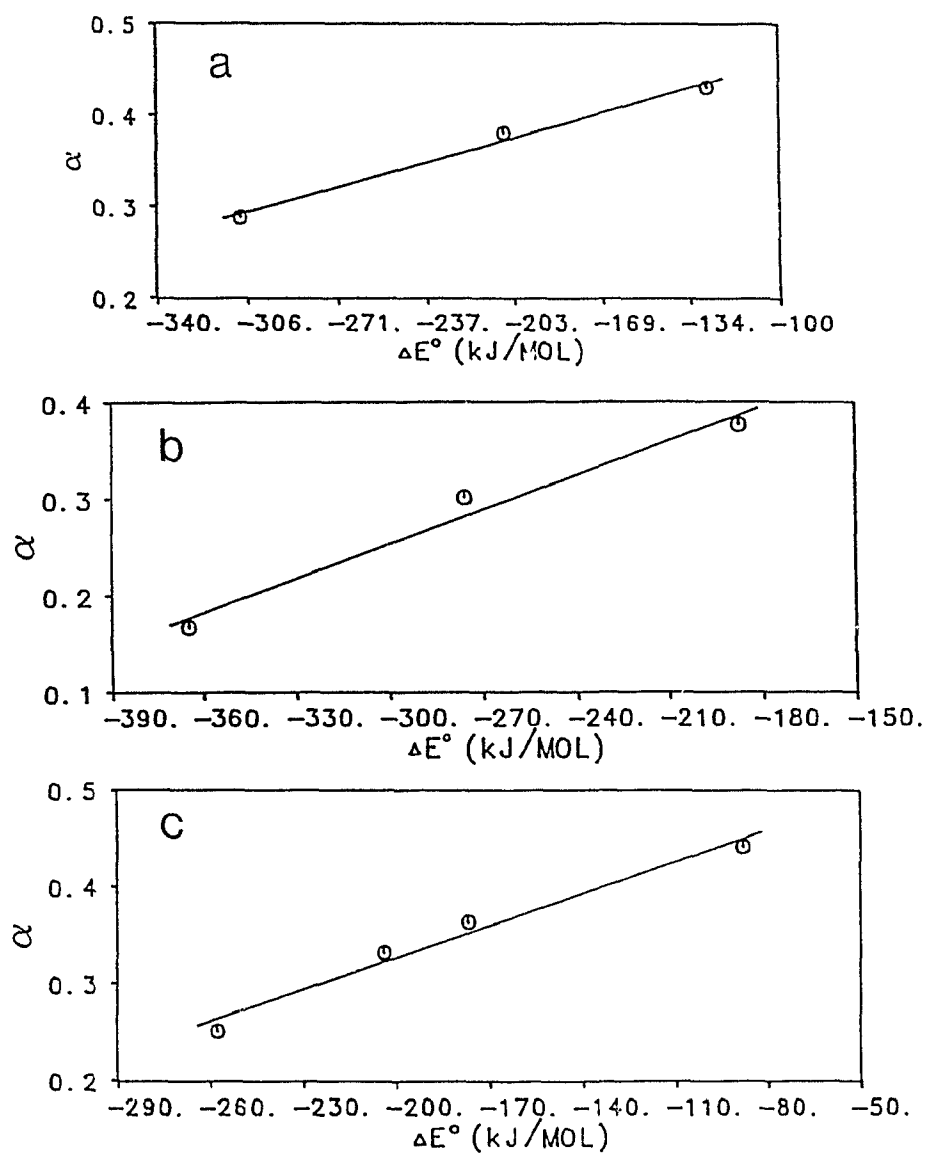


Figure 4.3.4 Plot of α values versus ΔE° for the reactions $\text{H}^- + \text{CH}_3\text{X} \rightarrow$

$\text{CH}_4 + \text{X}^-$. a) $\text{X} = \text{CCH}$, $\underline{\text{CN}}$ and $\underline{\text{NC}}$; b) $\text{X} = \text{PH}_2$, SH and Cl ;

c) $\text{X} = \text{NH}_2$, OH , OOH and F .

and

$$f_P = \frac{R_{C-n(TS)} - R_{C-n(Ground)}}{R_{C-n(Ground)}} \quad (4.3.10)$$

where $R_{C-X(TS)}$ is the C-X bond length at the TS. To normalize the geometry change, a parameter R_α is introduced

$$R_\alpha = \frac{f_R}{f_R + f_P} \quad (4.3.11)$$

Thus, if the TS resembles the reactant more than the product, $f_R < f_P$ and $R_\alpha < 0.5$. Otherwise, $R_\alpha > 0.5$. A plot of R_α versus α is shown in Fig. 4.3.5 in which the ground state is taken to be the ion-molecule complex and the reactions have the same nucleophile $N = H$ and the results are obtained at the MP2 level.

In summary, the α values obtained from linear plots should be interpreted with caution. It is only under the circumstances where the α' value is small that the α value obtained from a linear plot can be used as an index of the position of the TS along the reaction coordinate. If a set of reactions are correlated by the Bunting and Stefanidis equation, the α values are an index of the position of the TS in the forward and reverse activation energy space. The α value can be used as index of the TS structure, if the geometry parameter chosen is the major cause of the reorganization energy.

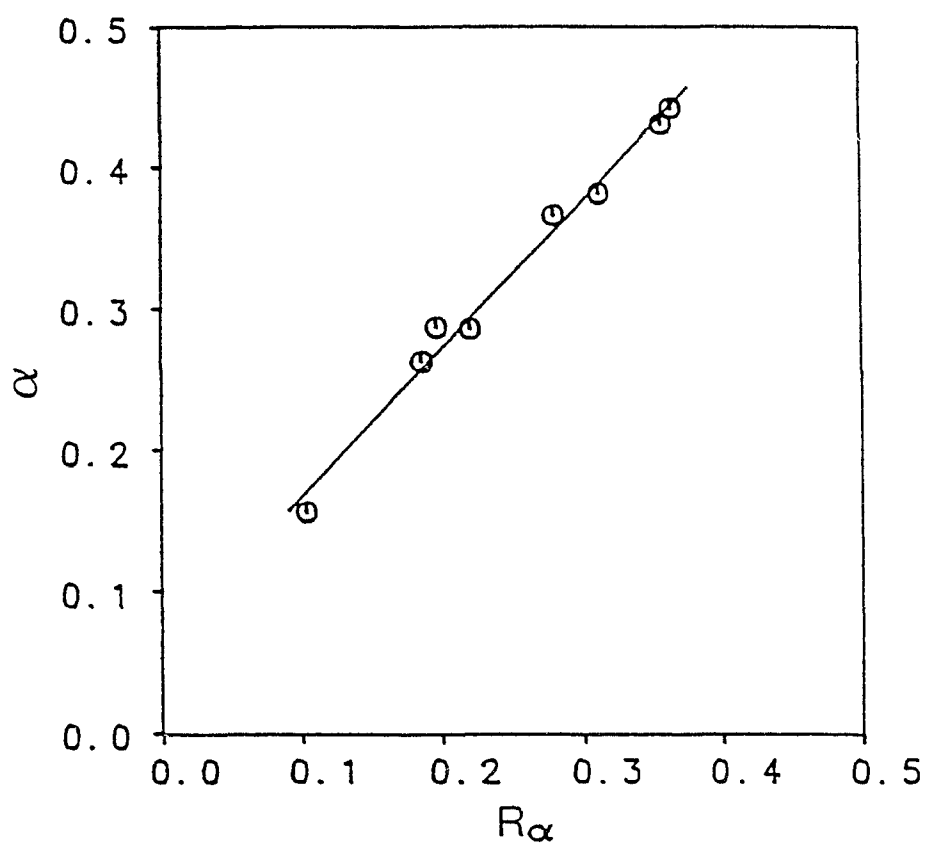


Figure 4.3.5 A plot of α versus R_α for the reactions $\text{H}^- + \text{CH}_3\text{X} \rightarrow \text{CH}_4 + \text{X}^-$

Chapter 5

The Laplacian of the Charge Density as a Probe in the study of Chemical Problems

5.1 Overview

Although the important property of the Laplacian of a scale function was first recognized as early as 1953 by Morse and Feshback,² more than twenty-five years passed before the Laplacian of the charge density was used to study chemical problems. Bader and co-workers^{1d,4b} showed that the Laplacian of the charge density identifies regions of space wherein the charge density is either locally concentrated or depleted. The Laplacian of the charge density reveals the existence of local concentrations of electronic charge in both the bonded and non-bonded regions of an atom in a molecule. It has also been found that the number, relative size and locations of the bonded and non-bonded charge concentrations in the valence shell of an atom in a molecule are in more or less general agreement with the localized pair model and with Gillespie's theory of molecular geometry.⁴ The form of the Laplacian of the charge density has been shown to reflect the shell structure of light atoms.^{1d,4b} For each principal quantum shell of an isolated atom, there are pairs of spherical shells of alternating charge concentration and charge depletion. Furthermore, there is a correspondence between the Laplacian of the charge density and frontier orbital theory since maximizing the overlap between the HOMO and LUMO of two reactants is equivalent to correlating the region of charge concentration in one

reactant with the region of charge depletion in the other.⁵

In this chapter, the Laplacian of the charge density is used to study the shell structure of atoms, electronegativity and nucleophilic substitution reactions in which the central atom is carbon or silicon. The purpose is not only to enhance our knowledge in these areas but also to show the advantages and disadvantages of using the Laplacian of the charge density in the study of chemical problems.

5.2 The Shell Structure of Free Atoms

The planetary model of the atom in which the electrons move in various orbits around the nucleus was proposed by Rutherford in 1911. Bohr further developed the model when he applied the concept of quantization of energy to the hydrogen atom.^{14b} According to the Bohr model, each electron moves in one of the orbits permitted by certain quantum conditions. Even though this simple picture is not retained by wave mechanics, it is useful to describe the electronic structure of atoms in terms of spherical shells denoted by *K*, *L*, *M*, etc..

To study the shell structure of free atoms, the radial density function $D(r)$, see eq. 5.2.1, has been used.

$$D(r) = r^2 \int \rho(r) d\Omega_r \quad (5.2.1)$$

where Ω_r is the angular coordinates of the electron. For the first three periods, the radial density function exhibits the expected numbers of spherical shells by showing corresponding numbers of maxima.⁶⁹ The existence of three maxima in $D(r)$ for Ar has been demonstrated by the

electron diffraction results of Bartell and Brockway.⁷⁰ However, for heavier atoms, only the inner shells which correspond to lower principal quantum numbers are revealed by $D(r)$.⁶⁹ A study done in momentum space indicates that the radial momentum distribution function does not reveal all occupied shells, but only the innermost ones (highest principal quantum number) which correspond to the outermost ones in position space.⁷¹ The Laplacian of the charge density in the atoms Li to Ne and Ar demonstrates the existence of corresponding shells in these atoms.^{1d,4b} However, further investigation is needed to see whether the Laplacian of the charge density can reveal all the shell structure of heavier atoms. For this purpose, the analytical Hartree-Fock wavefunctions of Clementi and Roetti⁷² were used for free atom calculations. A program was written to calculate the critical point of the Laplacian of the charge density ($\nabla(\nabla^2\rho(\mathbf{r})) = 0$). The calculations were carried out on the Perkin-Elmer 3230 computer.

The Laplacian of the charge density is defined as:

$$\nabla^2\rho(\mathbf{r}) = \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2} \quad (1.3.1)$$

A free atom has spherical symmetry and therefore the charge density is constant on a spherical surface whose centre is at the nucleus. Consider such a spherical surface of constant density. An axis, say the z axis, through the nucleus is normal to the surface and intersects it at the point $(0,0,z)$. Since the charge density decreases monotonically with increasing z , $\partial\rho/\partial z < 0$ and, in general, the curvature is found to be positive, that is, $\partial^2\rho/\partial z^2 > 0$. Thus, $\rho(0,0,z)$ is less than the average

of its values at the points $(0,0,z \pm dz)$. However, in the tangent plane, the charge density is a maximum at $(0,0,z)$, $\partial\rho/\partial x = \partial\rho/\partial y = 0$ and $\partial^2\rho/\partial x^2 = \partial^2\rho/\partial y^2 < 0$. Thus $\rho(0,0,z)$ is greater than the average of its values at $(\pm dx, \pm dy, z)$. If the sum of the magnitudes of the two negative curvatures exceeds the value of the positive curvature, then $\nabla^2\rho(0,0,z) < 0$, and the value of $\rho(0,0,z)$ is greater than the average of ρ at all points neighboring $(0,0,z)$. The charge density is concentrated at this point relative to its value averaged over all neighboring points. By determining a radius in an atom at which $\nabla^2\rho(r)$ is a minimum (or a maximum), it is possible to determine a radius at which electronic charge is maximally concentrated (or depleted). Because the atomic integral over all space of the Laplacian of the charge density of a free atom must vanish, there exist alternating minima and maxima in $\nabla^2\rho$. In other words, in addition to regions where the contraction of $\rho(r)$ along radial lines toward the nucleus is dominant and $\nabla^2\rho(r) > 0$, there must exist regions in which $\nabla^2\rho(r) < 0$. On the basis of calculations for a few light atoms, Li through Ne and Ar, it has been suggested that $\nabla^2\rho(r)$ exhibits pairs of regions, one negative and one positive, for each principal quantum shell. Thus $\nabla^2\rho(r)$ is said to exhibit the shell structure of atoms with each shell separated by a spherical node in $\nabla^2\rho(r)$. In each case, $\nabla^2\rho(r) < 0$ in the innermost region and a maximum of charge concentration is observed at the position of the nucleus.

Given that a region of charge concentration and one of charge depletion correspond to each principal quantum shell, the shell structure can be revealed by finding all radii corresponding to minima in $\nabla^2\rho(r)$. For every free atom, the charge density is a maximum at the

position of the nucleus and $\nabla^2\rho(r)$ is a minimum at $r_1 = 0$. Table 5.2.1 lists the calculated radii of minima in $\nabla^2\rho$ for the atoms from Li to Xe. In each case the minimum at the nucleus, r_1 , is omitted. In Table 5.2.1, r_i is the radius of the i th minimum in $\nabla^2\rho$. For the H and He atoms the only minimum in $\nabla^2\rho$ occurs at the position of the nucleus.

From the data in Table 5.2.1, it is clear that two minima are obtained for the atoms Li through Ne, corresponding to K and L shells. For the third period elements, Na to Ar, the third minimum corresponds to the M shell. In the fourth period, the N shell is discernible from the properties of $\nabla^2\rho(r)$ for K and Ca. From Sc ($Z = 21$) to Ge ($Z = 32$) the N shell is not distinguishable from the M shell. The M and N shells separate in As ($Z = 33$). The pattern is very similar in the fifth period: five shells are observed for Rb ($Z = 37$) and Sr ($Z = 38$), but from Y ($Z = 39$) to Te ($Z = 52$) only four shells are observed. The resolution of the N and O shells is regained in I and Xe.

From the preceding discussion it may be concluded that the form of the Laplacian of the charge density reflects the shell structure of the first twenty atoms. For the heavier atoms, the complete shell structure is resolved for the s -block elements and the later p -block elements, but only the inner shells are resolved in the d -block elements. Furthermore, the sign of the Laplacian of the charge density at the outermost minimum is reversed in those atoms of the fourth and fifth periods for which the full shell structure is resolved, the one exception being Kr. These observations emphasize that the resolution of the shell structure of heavy atoms is less complete than implied by the results of light atoms.⁷³

Table 5.2.1 Radii of minima in the Laplacian of the charge density of
the spherical atoms Li to Xe^a

Atom	State	r_2	r_3	r_4	r_5
Li	2_S	2.494 0.002			
Be	1_S	1.594 0.027			
B	2_P	1.188 0.141			
C	3_P	0.942 0.506			
N	4_S	0.776 1.447			
O	3_P	0.658 3.480			
F	2_P	0.569 7.592			
Ne	1_S	0.500 15.29			
Na	2_S	0.442 29.99	3.436 1.5E-4		
Mg	1_S	0.396 55.61	2.549 0.002		
Al	2_P	0.359 96.15	2.081 0.009		
Si	3_P	0.327 157.4	1.760 0.038		
P	4_S	0.301 247.4	1.522 0.115		
S	3_P	0.278 375.3	1.341 0.273		
Cl	2_P	0.258 553.3	1.198 0.592		
Ar	1_S	0.241 794.7	1.080 1.196		

Table 5.2.1 (continued)

Atom	State	r_2	r_3	r_4	r_5
K	2_S	0.226 1115	0.981 2.219	4.938 -3.1E-5	
Ca	1_S	0.213 1544	0.898 3.818	3.773 -1.2E-4	
Sc	2_D	0.201 2067	0.834 5.804		
Ti	3_F	0.190 2712	0.779 8.478		
V	4_F	0.181 3507	0.731 12.05		
Cr	5_D	0.172 4433	0.691 15.84		
Mn	6_S	0.165 5614	0.652 22.71		
Fe	5_D	0.158 6993	0.618 30.39		
Co	4_F	0.151 8648	0.587 39.84		
Ni	3_F	0.145 10554	0.559 51.67		
Cu	2_S	0.140 12705	0.535 63.72		
Zn	1_S	0.134 15398	0.510 83.76		
Ga	2_P	0.130 18494	0.487 109.0		
Ge	3_P	0.125 22126	0.466 140.2		
As	4_S	0.121 26303	0.446 179.7	2.175 -0.026	
Se	3_P	0.117 31124	0.427 226.9	1.833 -0.025	

Table 5.2.1 (continued)

Atom	State	r_2	r_3	r_4	r_5
Br	2_P	0.113 36615	0.410 288.3	1.652 -0.010	
Kr	1_S	0.110 42961	0.394 361.4	1.503 0.052	
Rb	2_S	0.106 49977	0.381 435.2	1.376 0.152	5.516 -3.5E-5
Sr	1_S	0.103 58191	0.367 541.4	1.278 0.275	4.369 -2.0E-4
Y	2_D	0.100 67246	0.354 653.7	1.204 0.517	
Zr	3_F	0.098 77430	0.342 788.6	1.140 0.879	
Nb	4_F	0.095 88851	0.331 943.2	1.082 1.438	
Mo	5_D	0.092 101420	0.320 1116	1.031 2.277	
Tc	6_S	0.090 115450	0.310 1320	0.984 3.450	
Ru	5_D	0.088 131010	0.301 1551	0.940 4.976	
Rh	4_F	0.086 148210	0.292 1807	0.901 7.074	
Pd	3_F	0.084 167080	0.284 2092	0.865 9.772	
Ag	2_D	0.082 187700	0.276 2413	0.830 13.22	
Cd	1_S	0.080 210880	0.269 2691	0.802 17.66	
In	2_P	0.078 236010	0.261 3186	0.770 23.23	
Sn	3_P	0.076 263580	0.254 3662	0.740 30.14	

Table 5.2.1 (continued)

Atom	State	r_2	r_3	r_4	r_5
Sb	$4S$	0.075	0.248	0.713	
		293890	4186	38.66	
Te	$3P$	0.073	0.242	0.688	
		327020	4779	48.91	
I	$2P$	0.072	0.236	0.665	2.228
		363180	5446	61.10	-0.037
Xe	$1S$	0.070	0.230	0.643	2.000
		402520	6184	76.09	-0.037

^a Each radius, r_i , is followed by the negative value of the Laplacian of the charge density at a radial distance r_i . All values are in atomic units.

Both the radial density function and the Laplacian of the charge density reveal the shell structure of light atoms. It should be stressed, however, that the radial density function reflects shell structure only through an averaging over the angular coordinates of the electrons to yield a one-electron distribution function, whereas the shell structure exhibited by the Laplacian distribution function is a property of the charge density in three-dimensional space. Also, it should be stressed that the charge density itself does not exhibit shell structure. For the atoms of the fourth and fifth periods, the number of shells distinguishable in $D(r)$ is always one or two less than the number expected on the basis of the ground state electron configurations.^{69c} The M and N shells do not give rise to separate maxima in $D(r)$ until $Z = 40$ is reached. Moreover, the indistinguishability of the N and O shells remains throughout the fifth period with only a slight shoulder for the O shell appearing in $D(r)$ for Xe.^{69c} In order to emphasize that $\nabla^2\rho(r)$ provides a more complete resolution of the shell structure of atoms than $D(r)$, Fig. 5.2.1 shows the r_i values obtained from minima in $\nabla^2\rho(r)$ and the r_i obtained from partitioning $D(r)$ as a function of atomic number. Fig. 5.2.1 also illustrates that where radii are obtained by both methods the results parallel one another closely.

5.3 Electronegativity

Electronegativity is of utmost importance to the chemist and chemical physicist. The concept of electronegativity finds its application in all fields of chemistry. Indeed, electronegativity is an inherent property of a species. However, the property is not directly measurable. The

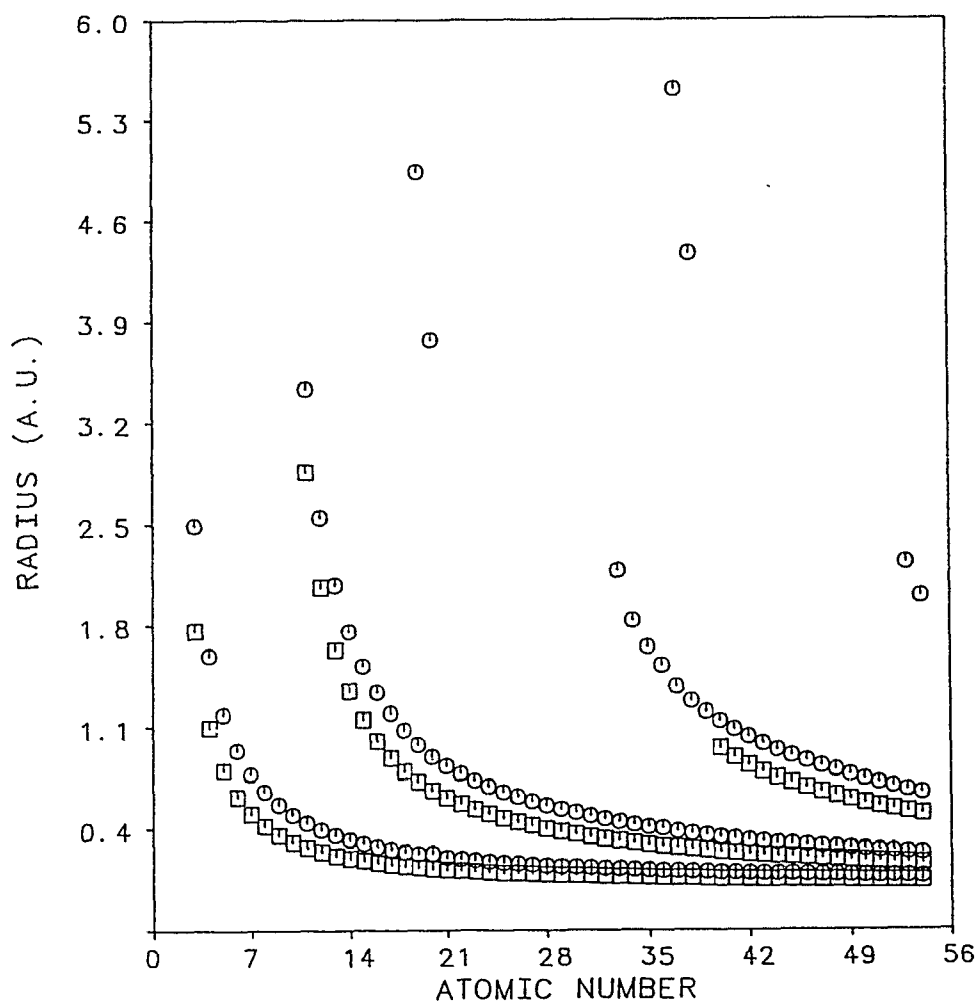


Figure 5.2.1 Radii (O) of minima in $\nabla^2 \rho(r)$ as a function of atomic number. For comparison radii (□) obtained from the partitioning of the radial density are plotted as a function of the atomic number.

original concept of electronegativity has been traced back to Pauling. He defined electronegativity "as the power of an atom in a molecule to attract electrons to itself".⁷⁵ There are several experimental scales of electronegativity.⁷⁴ Unfortunately, it has been very difficult to arrive at a unique unequivocal quantitative scale of electronegativity. Parr and co-workers⁷⁶ proposed a definition of electronegativity based on the quantum mechanical theorems of Hohenberg and Kohn, according to which electronegativity is equal to the negative of the electronic chemical potential, the latter being the derivative of the energy E with respect to the number of electrons in the species, with the external potential being held fixed. Several other theoretical studies of electronegativity have been reported in the literature.⁷⁷ It is the intention of this section to show that the property of the Laplacian of the charge density can be used to define the relative size of free atoms and to study the property of electronegativity. .

According to Pauling's definition electronegativity is a property of an atom in a molecule. Upon molecule formation, the differences in the electronegativities of atoms and groups of atoms cause the shift of electrons. As a result, some atoms gain electrons while others lose electrons. At the end, the electronegativities of the various atoms are equalized. The electron redistribution will certainly affect the size of atoms. Furthermore, this size change is related to the electronegativity of the atoms involved. In a diatomic molecule, the equilibrium bond length $r_e(AB)$ is directly related to the size of atoms A and B. Hence, a quantity $S(AB)$ is defined which measures the size change of atoms A and B upon formation of the molecule. Therefore, it should provide

information about the electronegativities of the atoms involved. The quantity $S(AB)$ is defined as

$$S(AB) = \frac{r_e(AB) - (r_A + r_B)}{(r_A + r_B)} \quad (5.3.1)$$

where $r_e(AB)$ is the equilibrium bond length of molecule AB and r_X is the relative size of free atom X . Equilibrium bond lengths are available from experimental data or from theoretical calculations whereas, in general, the relative radii of free atoms are not available from experiments and can be obtained from theoretical calculations. For this purpose it is helpful to recall from the discussion in the last section, that the Laplacian of the charge density reveals the shell structure of an atom. For each shell, there is a local minimum and a local maximum radius in $\nabla^2\rho$, and there is a zero (a radius at which $\nabla^2\rho = 0$) between the minimum and maximum radii. This zero is called the odd numbered zero because if the zeros are numbered from the nucleus outward then each even numbered zero lies between a maximum and a minimum which do not belong to the same shell, whereas each odd numbered zero lies between a minimum and a maximum which belong to the same shell (see Fig. 5.3.1). The properties of the Laplacian of the charge density can be used to obtain a definition of the relative size of an atom. For example, the radius of the outermost maximum, minimum or odd numbered zero of the Laplacian of the charge density can be used as an index of the relative size of an atom. Sagar *et al.*⁷⁸ reported that the radius of the outermost odd numbered zero of the Laplacian of the charge density exhibits a good correlation with the Bohr theory of an atom. Table 5.3.1

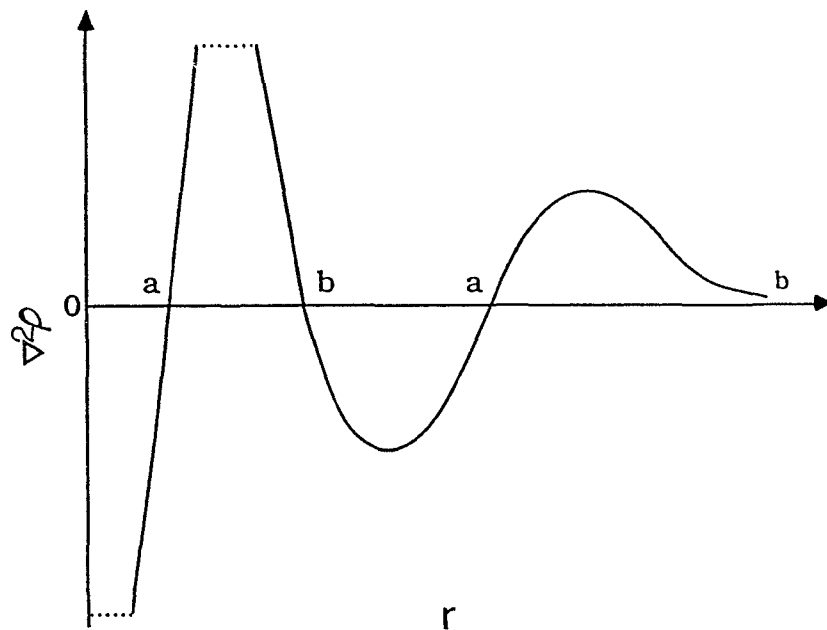


Figure 5.3.1 Schematic plot of $\nabla^2\rho(r)$ versus r for a free atom which has K and L shells. a) odd numbered zero; b) even numbered zero.

Table S.3.1 Radii of the outermost minimum, odd zero and maximum in $\nabla^2\rho$.

Atom	$r_{\min}^a$	r_{odd}^b	$r_{\max}^c$
Li	2.494	3.670	4.562
Be	1.594	2.403	2.980
B	1.188	1.783	2.219
C	0.942	1.404	1.754
N	0.776	1.153	1.446
O	0.658	0.973	1.224
F	0.569	0.840	1.058
Na	3.436	3.927	4.947
Mg	2.549	2.973	3.713
Al	2.081	2.542	3.131
Si	1.760	2.241	2.741
P	1.522	1.991	2.425
S	1.341	1.780	2.165
Cl	1.198	1.610	1.954

^a Radius (a.u.) corresponds to the outermost minimum in $\nabla^2\rho$.

^b Radius (a.u.) corresponds to the outermost odd numbered zero of $\nabla^2\rho$.

^c Radius (a.u.) corresponds to the outermost maximum in $\nabla^2\rho$.

lists the radii corresponding to the outermost minimum, odd numbered zero and maximum of $\nabla^2\rho$ for free atoms. In the following discussion the three types of radii are used as indices of the size of free atoms.

First of all, let us discuss how the values of $S(AB)$ change with the electron attracting ability of atoms A and B. Suppose we have a molecule, AB, in which the ability of atom B to attract electrons is much higher than that of atom A. Let us further suppose that in forming the molecule, atom A loses one electron, while atom B gains one electron. Such would be the case if atom A is a group IA element, and atom B is a group VIIA element. Since atom A loses a valence electron, its valence shell disappears, while for atom B, the valence shell is completed (see Fig. 5.3.2). Therefore, we would expect that the equilibrium bond length of molecule AB ($r_e(AB)$) is shorter than the sum of the outermost shell radii of the two atoms and, therefore, $S(AB) < 0$. If the electron attracting ability of atom A increases so that the difference between the electron attracting abilities of the two atoms is small, then electrons are shared by the two atoms rather than being transferred (see Fig. 5.3.3). In this situation, no shell annihilation occurs. Consequently we would predict the equilibrium bond length $r_e(AB)$ to be longer than the sum of the outermost minimum radii of the free atoms, $S(AB) > 0$. With a further increase of the electron attracting ability of atom A, the value of $S(AB)$ would increase further.

On the basis of the above discussion, it is reasonable to assume that $S(AB)$ provides a measure of the electronegativity of atom A relative to atom B. In order to test this hypothesis, Table 5.3.2 presents calculated values of $S(AF)$ where the experimental bond lengths of the

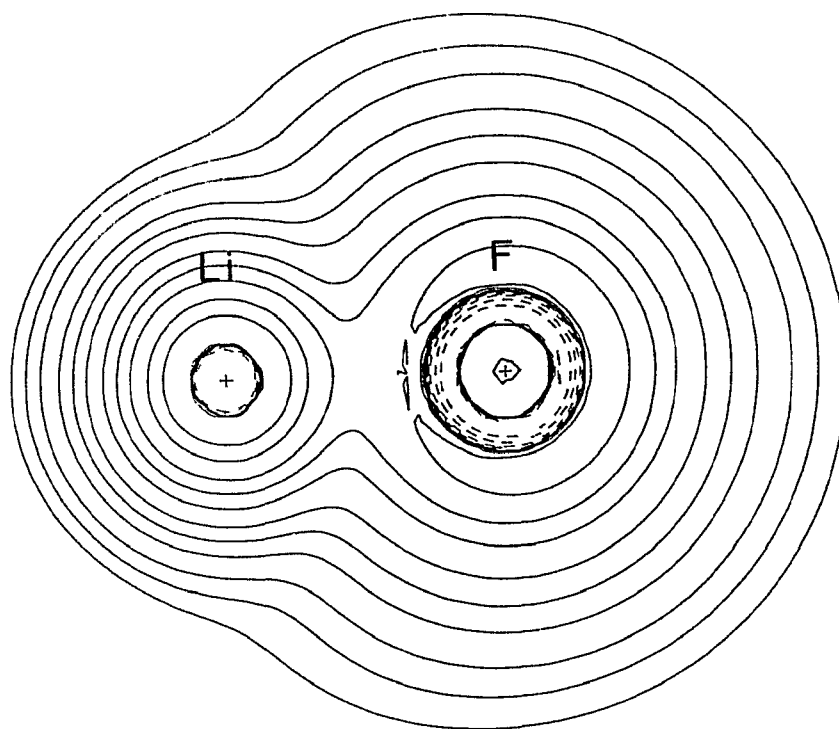


Figure 5.3.2 $\nabla^2\rho$ contour map of LiF. Dotted line corresponds to regions in which $\nabla^2\rho < 0$; solid line corresponds to regions in which $\nabla^2\rho > 0$. Only the inner shell of Li is observed.

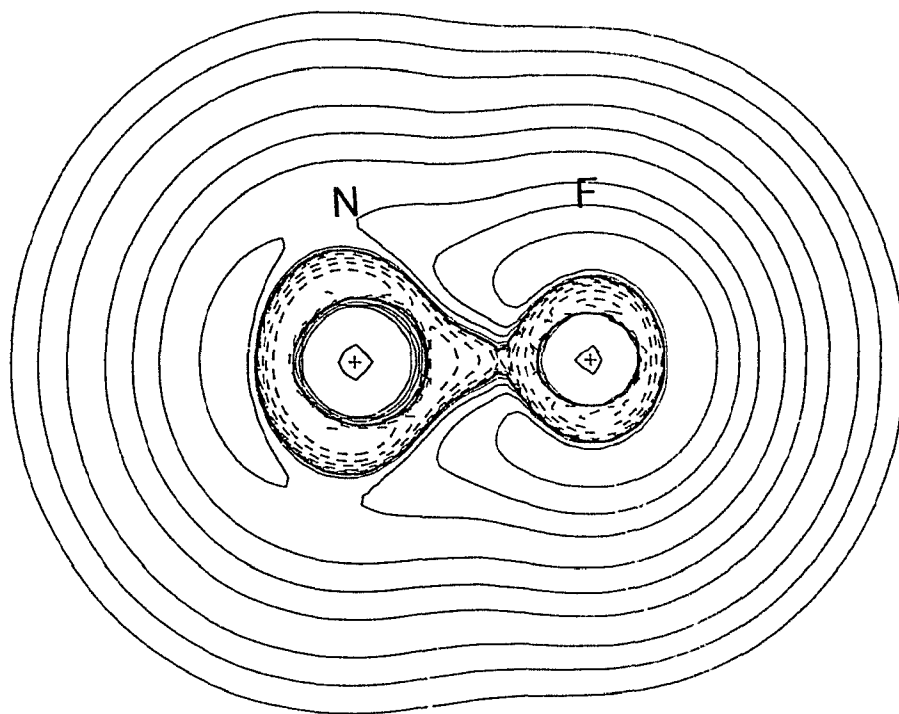


Figure 5.3.3 $\nabla^2 \rho$ contour map of NF. Valence shells of both atoms are observed and there is a charge concentration in the bonding region ($\nabla^2 \rho < 0$).

Table 5.3.2 S(AF) values obtained from various radii.

Atom	S(AF) ^a	S(AF) ^b	S(AF) ^c	χ_A^d
Li	-0.035	-0.345	-0.474	1.04
Be	0.189	-0.207	-0.363	1.55
B	0.358	-0.091	-0.272	1.93
C	0.591	0.071	-0.145	2.46
N	0.850	0.249	-0.006	3.04
O	1.042	0.382	0.098	3.47
F	1.344	0.588	0.261	4.16
Na	-0.091	-0.237	-0.394	1.10
Mg	0.061	-0.133	-0.307	1.26
Al	0.130	-0.076	-0.254	1.41
Si	0.299	-0.018	-0.204	1.80
P	0.437	0.061	-0.138	2.11
S	0.583	0.155	-0.061	2.44
Cl	0.741	0.256	0.021	2.79

^a Obtained using $r_{\min}$ in Table 5.3.1.

^b Obtained using r_{odd} in Table 5.3.1.

^c Obtained using $r_{\max}$ in Table 5.3.1.

^d Obtained from eq. 5.3.2.

diatomic fluorides are taken from the compilation of Huber and Herzberg.⁷⁹ The bond lengths for LiF through F₂ and NaF through ClF are 1.564, 1.361, 1.263, 1.272, 1.317, 1.326, 1.412, 1.926, 1.750, 1.654, 1.601, 1.590, 1.601 and 1.628 angstroms. The Pauling, Sanderson and Allred-Rochow electronegativities of atom A correlate linearly with the computed S(AF) values of the diatomic fluorides, as shown in Fig. 5.3.4, 5.3.5 and 5.3.6, respectively, where the S(AF) values are obtained by taking the radius of the outermost minimum as the relative size of free atoms. The respective correlation coefficients are 0.991, 0.982 and 0.998. The correlation with the Allred-Rochow electronegativities is especially strong.

Linear regression analysis of the data in Fig. 5.3.6 leads to the following equation

$$\chi_A = 2.26 \frac{r_e(AF) - (r_A + r_F)}{(r_A + r_F)} + 1.12 \quad (5.3.2)$$

In effect eq. 5.3.2 converts the S(AF) values to electronegativities on the Allred-Rochow scale. This formula can also be used to predict the equilibrium bond length of molecule AF given r_A and r_F , and the electronegativity of atom A in the molecule. In addition,, the radius of the outermost minimum of an element can be estimated from eq. 5.3.2, provided an estimate of $r_e(AF)$ is available.

Allred-Rochow electronegativities are plotted against S(AF) values calculated by using the radius of outermost maximum as the relative size of a free atom in Fig. 5.3.7. Clearly the correlation is weaker than in Fig. 5.3.6 where the radius of the outermost minimum is used as the

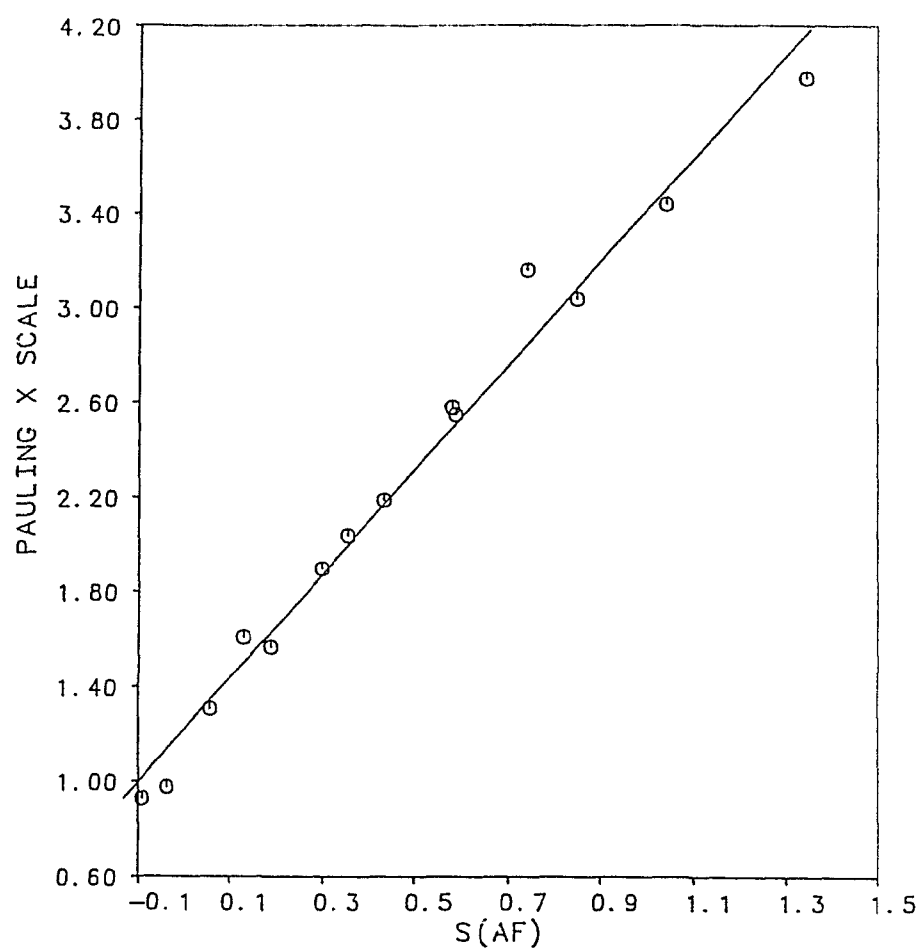


Figure 5.3.4 Plot of Pauling electronegativities versus $S(AF)$ values
obtained from the radius of the outermost minimum in V_p^2 .

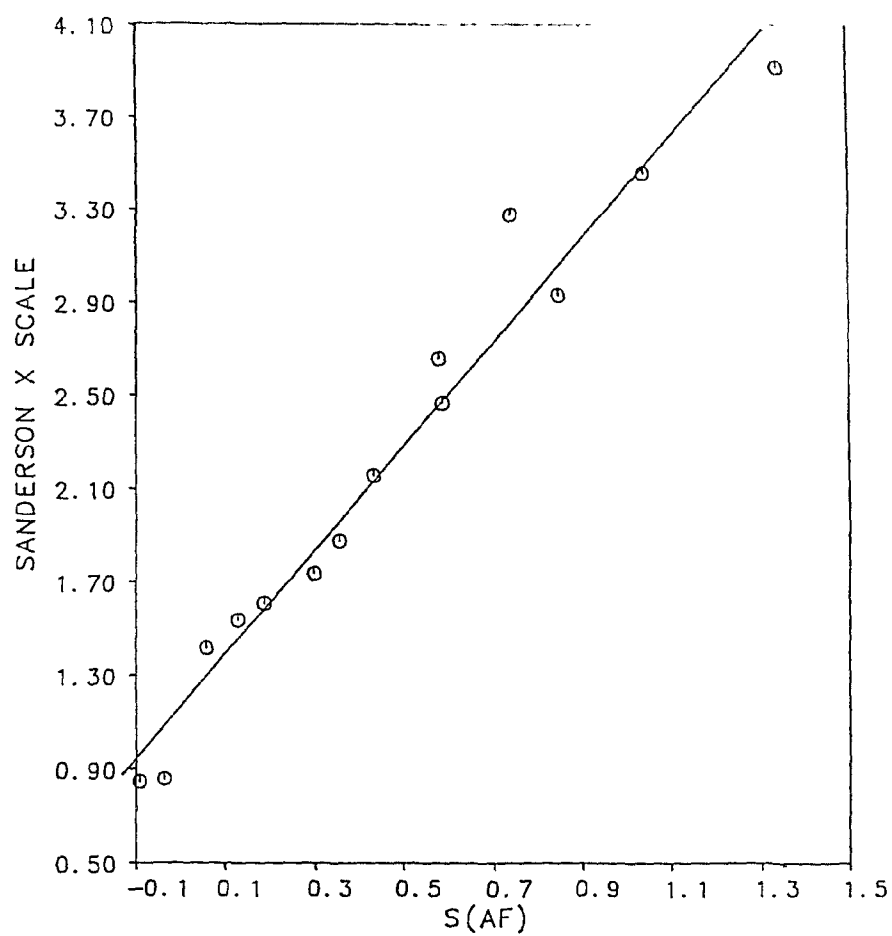


Figure 5.3.5 Plot of Sanderson electronegativities versus $S(AF)$ values
obtained from the radius of the outermost minimum in $\nabla^2\rho$.

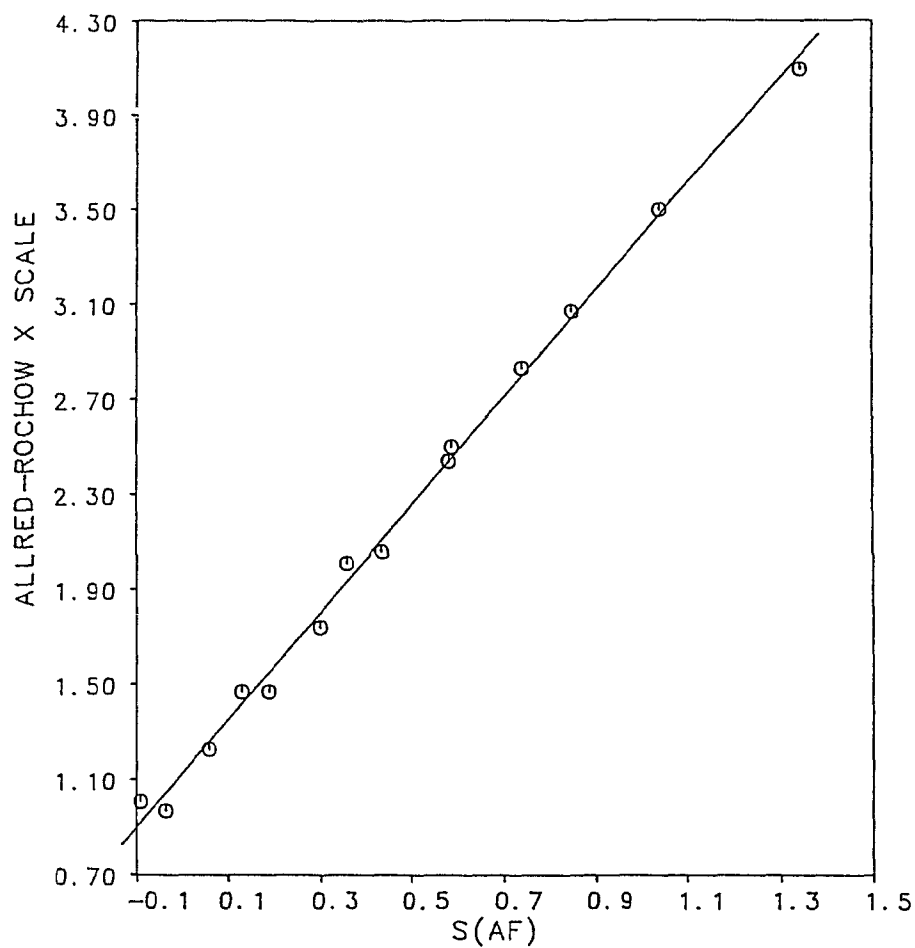


Figure 5.3.6 Plot of Allred-Rochow electronegativities versus $S(\text{AF})$
 values obtained from the radius of the outermost minimum
 in $\nabla^2\rho$.

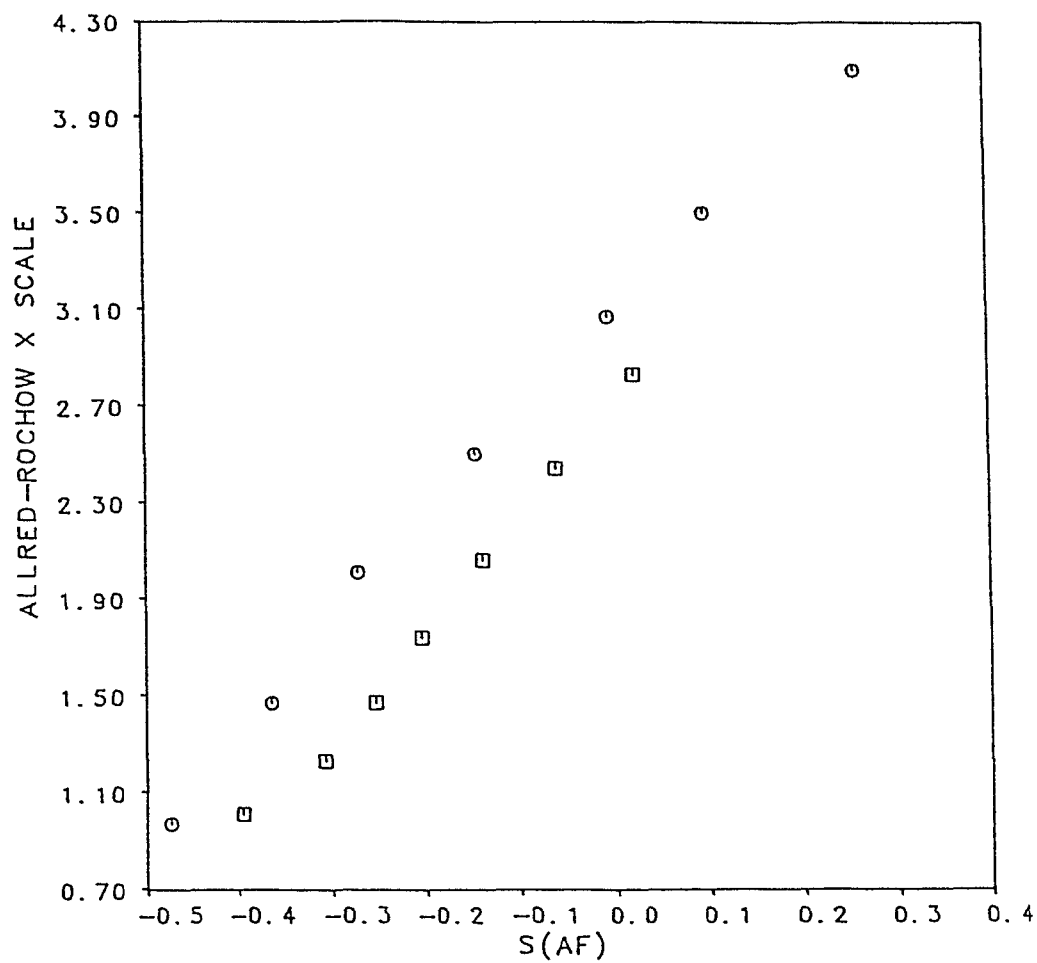


Figure 5.3.7 Plot of Allred-Rochow electronegativities versus $S(AF)$

values obtained from the radius of the outermost maximum in $V^2\rho$. (○) indicates the first-row element and (□) indicates the second-row element.

relative size of a free atom. Fig. 5.3.8 shows the plot of Allred-Rochow electronegativities versus the $S(AF)$ values obtained by using the radius of the outermost odd numbered zero as the relative size of free atoms. Here again, the correlation is not as good as that in Fig. 5.3.6. Thus, using the radius of the outermost minimum in $\nabla^2\rho(r)$ as the relative size of free atoms gives the best correlation with the Allred-Rochow electronegativity scale, which is the widely accepted one.⁷⁴ $S(AF)$ values obtained by using the outermost maximum or odd numbered zero suggest that the difference in electronegativities between first-row and second-row elements should be smaller than indicated by the Allred-Rochow scale. Unless the suggestion is true, the choice of the radius of the outermost minimum as the relative size of a free atom is the best one. The fact that the outermost minimum provides information about the relative size change of an atom in the molecule is also illustrated in Fig. 5.3.9 where the $\nabla^2\rho$ maps for free atom F and molecule BF are shown. Since all free atoms have spherical symmetry, a spherical shell with $\nabla^2\rho < 0$ is observed in F. In molecule BF the valence shells of B and F are distorted so that the valence shell $\nabla^2\rho < 0$ regions are no longer spherical. The radius of the outermost minimum corresponds to the region of valence shell charge concentration in which the major chemical changes occur.

5.4 S_N2 Reactions at Carbon and Silicon

The chemistry of first-row elements differs considerably from that of the second-row elements. The differences are exhibited in the bonding arrangement, molecular stabilities, reaction processes and other

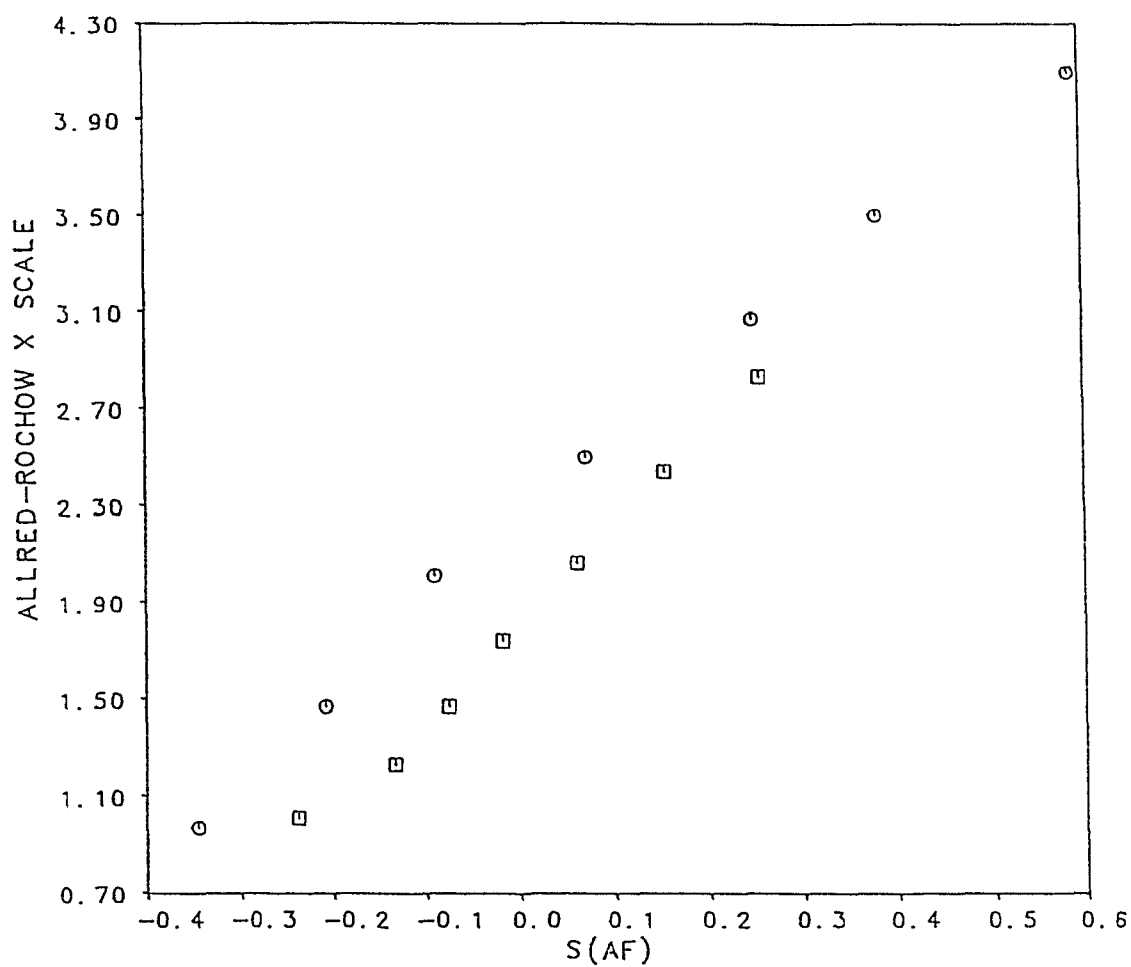


Figure 5.3.8 Plot of Allred-Rochow electronegativities versus $S(AF)$ values obtained from the radius of the outermost odd numbered zero in $\nabla^2\rho$. (○) indicates the first-row element and (□) indicates the second-row element.

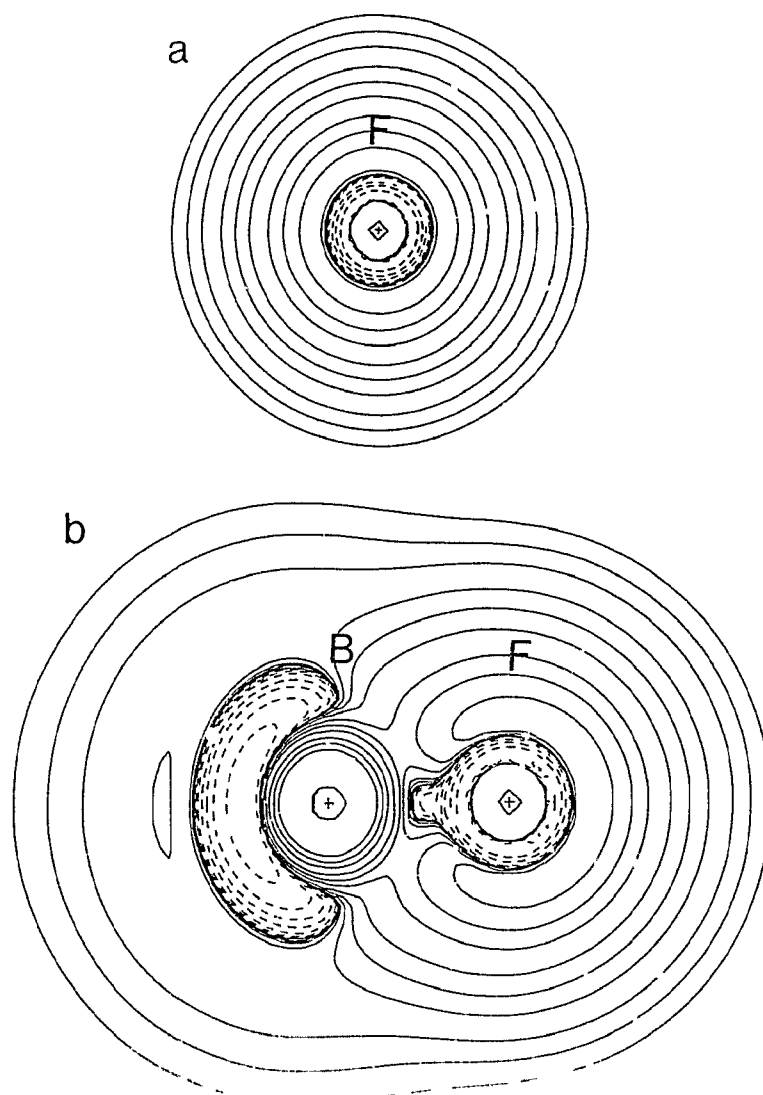


Figure 5.3.9 Contours of $V^2 \rho$, a) F b) BF.

properties. Such effects are normally attributed to the so called d -orbital effect.⁸⁰ For second-row elements, d -orbitals can be used to form bonds while for the first-row elements, this is not possible. Nevertheless, the explanation needs to be proven. Recent success in synthesizing conjugated compounds of second-row elements⁸¹ is a challenge to the classical belief that second-row elements can not form delocalized π -bonds which are common for first-row elements. In this section, the focus is on the different reaction pathways for first-row and second-row elements. To be more specific, the bimolecular nucleophilic substitution reactions of carbon and silicon are considered.

Bimolecular nucleophilic substitution reactions with carbon at the center ($S_N2(C)$) invariably take place by an inversion process. In the gas phase, the potential energy surface has a double well shape and the pentacoordinated carbon is the transition state. However, a considerable body of evidence has been accumulated⁸² showing that bimolecular substitution reactions at tetracoordinated silicon ($S_N2(Si)$) proceed via a pentacoordinated intermediate and that both the retention and inversion processes compete with one another. The reactions exhibit a V shape potential energy surface with the pentacoordinated silicon at the bottom of the energy surface. Furthermore, the reaction at silicon is considerably faster than at carbon. Studies indicate that the stabilization of pentacoordinated silicon is not due to the d -orbitals and the destabilization of pentacoordinated carbon is attributed to the small size of the carbon atom and hence to the crowded packing of the ligands.^{82e} The retention process (front-side attack) is explained^{82d} by

increasing the favorable interaction between the nucleophile and Si and/or decreasing the unfavorable interaction between the nucleophile and the leaving group. To gain further insight into differences in $S_N2(C)$ and $S_N2(Si)$ reactions, the Laplacian of the charge density is employed in this thesis. It has been suggested that the Laplacian of the charge density can be used to study chemical reactivity.⁵ The initial approach of the reactants can be determined by aligning regions of local charge concentration with regions of local charge depletion as determined by the Laplacian of the charge density. Thus, the Laplacian of the charge density of CH_3X and SiH_3X molecules has been calculated, where the leaving group X is H, NH_2 , OH, OOH, F, PH_2 , SH, Cl, CCH, CN or NC for CH_3X and H, OH, F, SH or Cl for SiH_3X . The calculations for SiH_3X are similar to those for CH_3X (see section 3.2), except that they are only carried out at the Hartree-Fock level.

Before discussing the results, it is helpful to review the properties associated with the extrema in $\nabla^2\rho$. As discussed earlier, the Laplacian of the charge density provides information about where in space the charge is concentrated or depleted. If $\nabla^2\rho < 0$, then the charge is concentrated in the region of space being considered. If $\nabla^2\rho > 0$, then the charge is depleted from the region of space. The local minimum in $\nabla^2\rho$ is the local minimum of charge depletion or the local maximum of charge concentration. The local maximum in $\nabla^2\rho$ is the local maximum of charge depletion.

The $\nabla^2\rho$ contour map of CH_3Cl is shown in Fig. 5.4.1. Two observations should be addressed. First of all, instead of a spherical valence-shell charge concentration, as observed in free atoms, the valence-shell

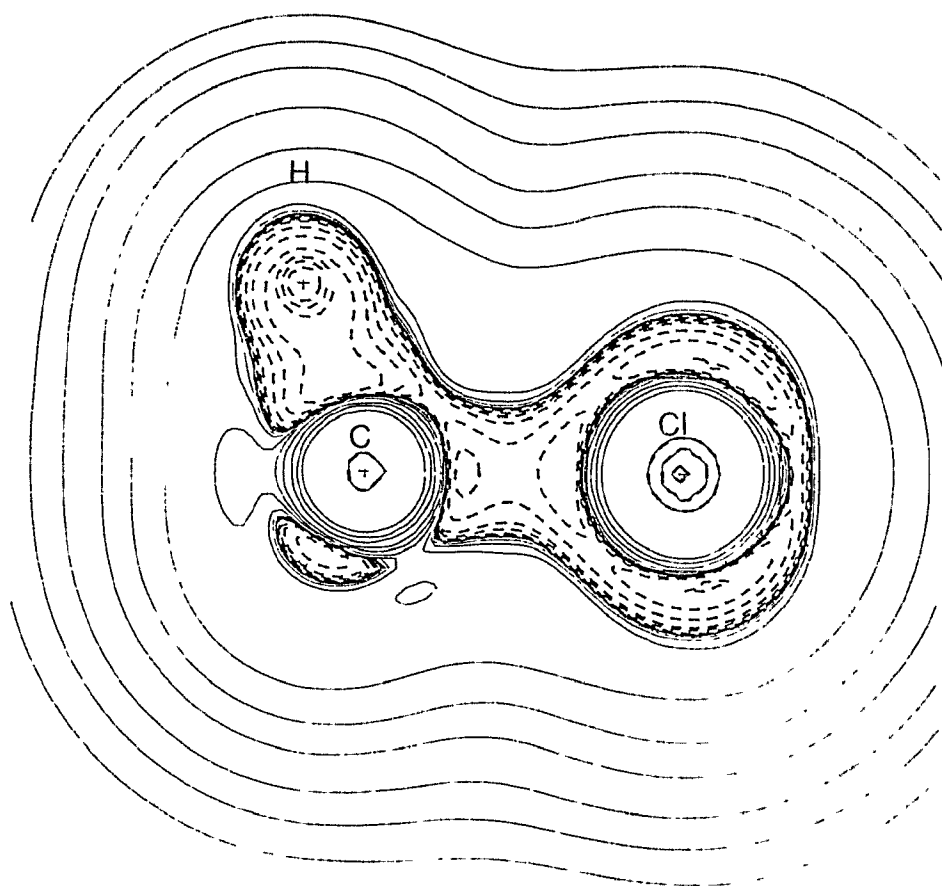


Figure 5.4.1 $V^2\rho$ contour map of CH_3Cl in the ClCH plane.

charge of carbon is distorted such that the valence-shell charge is concentrated along each bond with H and Cl ($\nabla^2\rho < 0$) and opposite to every bond, there is a valence-shell charge depletion region ($\nabla^2\rho > 0$). Secondly, the C-H and C-Cl bonds are predominantly covalent as shown by the charge concentration regions between bonded atoms ($\nabla^2\rho < 0$). This may be compared with the predominantly ionic bond illustrated in Fig. 5.3.2, where the charge is depleted from the bonding region ($\nabla^2\rho > 0$).

Calculations of the valence-shell charge concentration⁵ (VSCC) of C in CH_3X show that there are four minima of $\nabla^2\rho$ (maximum charge concentration), each located along the bond path and there are four maxima in $\nabla^2\rho$ (maximum charge depletion), each located opposite to the bond. The values of VSCC are listed in Table 5.4.1. For all the CH_3X molecules studied, the values of the nonbonding maxima opposite to the C-X bond are larger than those opposite to the C-H bond, which means that the charge is more depleted in the region opposite to the C-X bond than in the region opposite to the C-H bond. It is also noted that the charge densities (ρ values) are different, though the differences are small, in these areas as well. The local maximum of $\nabla^2\rho$ opposite to the C-X bond has a even smaller charge density than that at the local maximum opposite to the C-H bond. Thus, the region opposite to the C-X bond is easier to subject to nucleophilic attack which explains why back side attack is observed in $\text{S}_{\text{N}}2(\text{C})$ reactions. According to Bader *et al.*,⁵ the region with the large maximum $\nabla^2\rho$ value corresponds to the LUMO of the molecule. Thus, the region opposite to the C-X bond is the region where the LUMO is mainly concentrated. The $\nabla^2\rho$ contour map of CH_3Li is shown in Fig. 5.4.2. Instead of charge depletion in the nonbonding area

Table 5.4.1 Extrema in VSCC of carbon in CH_3X (a.u.).

CH_3X	CY	CY bond minima			Associated maxima			$\Delta(\nabla^2\rho_{\text{max}})^d$
		r^a	ρ^b	$\nabla^2\rho^c$	r	ρ	$\nabla^2\rho$	
CH_3H	CH	0.969	0.295	-1.177	1.008	0.170	0.117	0.000
		(1.014	0.296	-1.246	1.009	0.169	0.081	0.000) ^e
CH_3CCH	CC	1.013	0.276	-0.958	1.019	0.166	0.158	0.025
	CH	0.960	0.302	-1.244	1.008	0.168	0.133	
CH_3CN	CC	1.029	0.268	-0.894	1.023	0.163	0.169	0.038
		(1.041	0.269	-0.910	1.017	0.163	0.134)	
	CH	0.956	0.306	-1.275	1.008	0.169	0.131	
		(1.000	0.307	-1.332	1.012	0.169	0.091	
CH_3NC	CN	1.096	0.265	-0.758	1.064	0.144	0.261	0.076
	CH	0.949	0.314	-1.371	1.021	0.158	0.185	
CH_3PH_2	CP	0.976	0.244	-0.805	1.011	0.170	0.108	0.032
	CH_1^f	0.965	0.298	-1.200	1.002	0.173	0.076	
	CH_2^g	0.967	0.296	-1.181	1.001	0.173	0.061	
	CH^h	0.966	0.297	-1.187	1.002	0.173	0.066	
CH_3SH	CS	1.003	0.222	-0.660	1.037	0.156	0.186	0.124
		(1.017	0.221	-0.666	1.026	0.157	0.148)	
	CH_1	0.958	0.305	-1.270	1.002	0.170	0.062	
		(1.001	0.306	-1.329	1.005	0.169	0.030	0.119)

Table 5.4.1 (continued)

CH_3X	CY	<u>CY bond minima</u>			<u>Associated maxima</u>			$\Delta(\nabla^2\rho_{\text{max}})$
		r	ρ	$\nabla^2\rho$	r	ρ	$\nabla^2\rho$	
CH_3SH	CH_2	0.957	0.306	-1.282	1.004	0.169	0.088	0.098
		(1.000	0.307	-1.342	1.008	0.168	0.057	0.052)
	CH	0.957	0.306	-1.278	1.003	0.169	0.079	0.107
		(1.000	0.307	-1.338	1.007	0.169	0.048	0.100)
CH_3Cl	CCl	1.038	0.197	-0.496	1.079	0.137	0.251	
		(1.052	0.197	-0.568	1.046	0.144	0.209)	
	CH	0.948	0.315	-1.377	1.010	0.162	0.096	0.155
		(0.990	0.316	-1.433	1.013	0.162	0.062	0.146)
CH_3NH_2	CN	1.021	0.276	-0.933	1.040	0.155	0.223	
								0.036
	CH_1	0.961	0.300	-1.246	1.016	0.160	0.187	
								0.089
	CH_2	0.958	0.305	-1.287	1.010	0.164	0.135	
								0.071
	CH	0.959	0.303	-1.273	1.012	0.163	0.152	
CH_3OH	CO	1.057	0.273	-0.741	1.076	0.139	0.281	
		(1.054	0.273	-0.728	1.043	0.146	0.235)	
	CH_1	0.950	0.314	-1.384	1.015	0.159	0.149	0.132
		(0.992	0.315	-1.437	1.015	0.159	0.116	0.119)
	CH_2	0.954	0.308	-1.331	1.022	0.155	0.198	0.083
		(0.998	0.308	-1.383	1.020	0.156	0.160	0.075)
	CH	0.952	0.310	-1.349	1.020	0.156	0.181	0.099
		(0.996	0.311	-1.401	1.019	0.157	0.145	0.090)

Table 5.4.1 (continued)

CH ₃ X	CY	CY bond minima			Associated maxima			$\Delta(\nabla^2\rho_{\max})$
		r	ρ	$\nabla^2\rho$	r	ρ	$\nabla^2\rho$	
CH ₃ OOH	CO	1.079	0.278	-0.732	1.091	0.133	0.284	0.124 0.088 0.100
	CH ₁	0.951	0.312	-1.372	1.012	0.160	0.160	
	CH ₂	0.949	0.313	-1.379	1.020	0.159	0.196	
	CH	0.949	0.313	-1.377	1.018	0.159	0.184	
CH ₃ F ⁱ	CF	1.057	0.152	-0.379				0.090
		(1.050	0.256	-0.442	1.065	0.134	0.277)	
	CH	0.944	0.319	-1.443	1.033	0.149	0.204	
		(0.986	0.319	-1.489	1.029	0.149	0.187	

^a Distance between extreme point and carbon (a.u.).

^b Charge density at extreme point (a.u.).

^c Value of the Laplacian of the charge density at the extreme point (a.u.).

^d The value is defined in eq. 5.4.1.

^e Values in parentheses are obtained from HF/[5s4p/3s]**//HF/6-31+G* calculations.

^f For molecules with C_s symmetry, there are two types of C-H bond. The C-H bond corresponds to the one which lies in the symmetry plane.

^g The C-H bonds correspond to the ones symmetric to the symmetry plane.

^h The average values of the three methyl C-H bonds.

ⁱ With the 6-31+G* basis set no local maximum was found in regions opposite to the C-F bond.

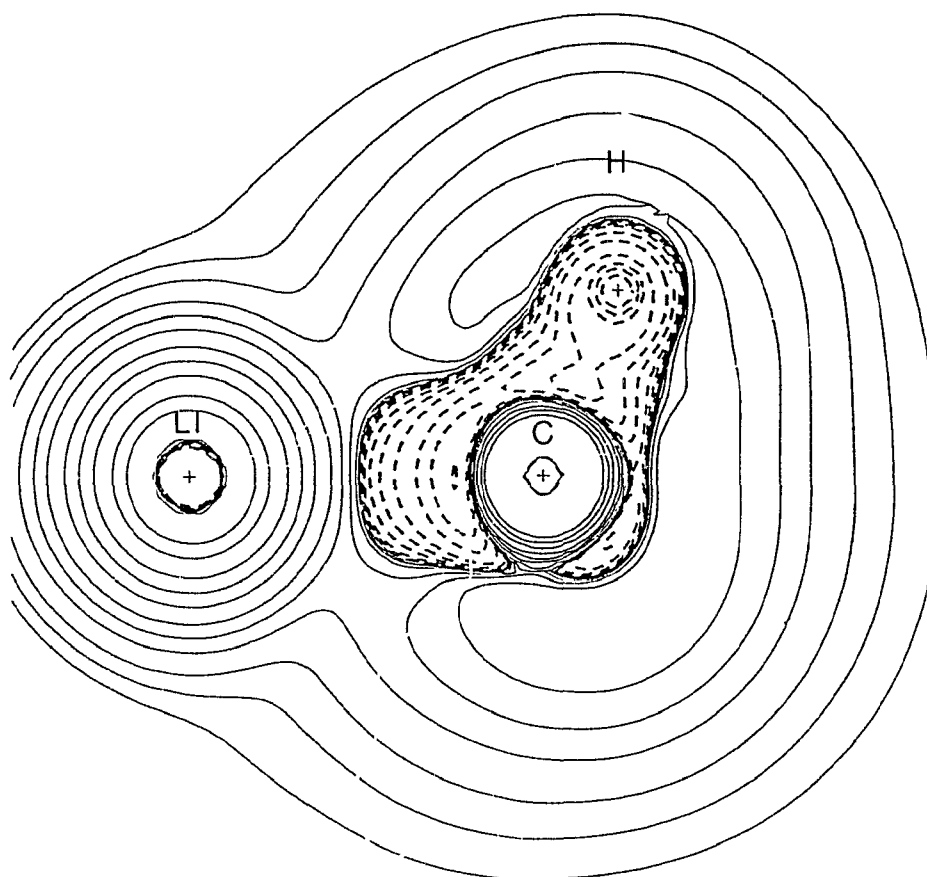


Figure 5.4.2 $\nabla^2 \rho$ contour map of CH_3Li in the HCLi plane.

opposite to the C-X bond, a negative value of the Laplacian of the charge density is observed in the region opposite to the C-Li bond. Hence, nucleophilic attack is favoured in the region opposite to the C-H bond where the charge is depleted (local maximum in $\nabla^2\rho = 0.035$) and the leaving group would be H.

Another important note from Table 5.4.1 is that the value of the nonbonding maximum of $\nabla^2\rho$ opposite to the C-X bond changes with X. Using the classification of X described in section 4.2, the value of $\nabla^2\rho$ correlates with the electronegativity of X within each group. Hence, it is correlated with the intrinsic barriers of the symmetric reactions $X^- + CH_3X \rightarrow X^- + CH_3X$ as well.

Thus, for $S_N2(C)$ reactions, due to the dominant covalent bonding feature, the valence-shell charge concentrations of carbon are directed toward each bond path and holes are created in regions opposite to each bond. The depth of the hole is related to the electronegativity of X. The greater the electronegativity of X, the greater the contribution of X to the bonding orbital. The contribution of carbon to the bonding orbital is correspondingly small and as a result, the C contribution to virtual orbital is large. Hence, the hole opposite to the C-X bond is deeper and it is the best target for nucleophilic attack. Also carbon is "reluctant" to form pentacoordinated species due to its covalent dominant bonding feature. thus, the pentacoordinated TS has a higher energy.

The $\nabla^2\rho$ contour map of SiH_3X is shown in Fig. 5.4.3. Comparison with Fig. 5.4.1, indicates the absence of the valence shell of Si. Valence-shell charge concentration calculations were performed for SiH_3X

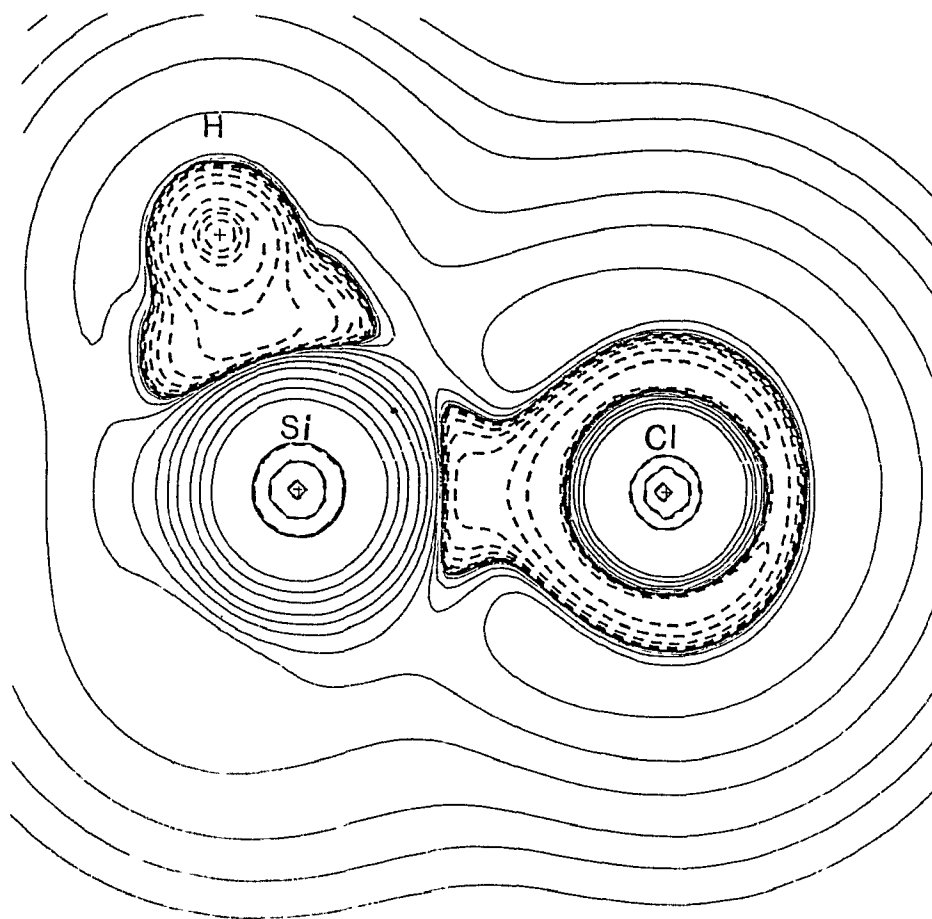


Figure 5.4.3 $\nabla^2 \rho$ contour map of SiH_3Cl in the ClSiH plane.

but no local maxima and no local minima of $\nabla^2\rho$ were found. Charge integration results using the molecular structure theory¹ are provided in Table 5.4.2. Comparison with the results for CH_3X (Table 4.2.3), indicates that the Si-H and Si-X bonds have more ionic character and that silicon has a charge of about +3. Obviously, the large positive charge makes nucleophilic attack much easier. This is one of the reasons why $\text{S}_{\text{N}}2(\text{Si})$ reactions are much faster. Moreover, the large positively charged center can attract a nucleophile from all directions and substituents effect are small. Thus, the reaction can proceed via both the retention and inversion processes. Furthermore, the predominantly ionic bonding involved with Si makes the pentacoordinated Si more stable. Thus, instead of having a pentacoordinated transition state as in the case of a $\text{S}_{\text{N}}2(\text{C})$ reaction, a $\text{S}_{\text{N}}2(\text{Si})$ reaction has a pentacoordinated intermediate, which lies at the bottom of the potential energy surface. This explains why the $\text{S}_{\text{N}}2(\text{Si})$ reactions are much faster.

Although, different substituents play a minor role in $\text{S}_{\text{N}}2(\text{Si})$ reactions, they do, however, affect the ratio of retention to inversion products or in another words the ratio of front- to back-side attacks. VSCC calculations of Si can not provide information about the ratio, as noted earlier. Nonetheless, an interesting relationship is observed between the ratio and VSCC study of CH_3X . Table 5.4.1 provides values of the difference between the local maximum of $\nabla^2\rho$ opposite to the C-X bond and that opposite to the C-H bond ($\Delta(\nabla^2\rho_{\text{max}})$)

$$\Delta(\nabla^2\rho_{\text{max}}) = \nabla^2\rho_{\text{max}(\text{b})} - \nabla^2\rho_{\text{max}(\text{f})} \quad (5.4.1)$$

Table 5.4.2 Integrated charges on atom X in SiH_3X (e).

SiH_3X	$-Q_{\text{H}}$	$-Q_{\text{X}}$
SiH_3H	0.726	0.726
SiH_3OH	0.734 ^a	0.866
SiH_3F	0.725	0.916
SiH_3SH	0.725 ^a	0.725
SiH_3Cl	0.720	0.791

^a Average charge on three methyl hydrogens.

where $\nabla^2\rho_{\max(b)}$ is the local maximum value of $\nabla^2\rho$ at the back side of the Si-X bond and $\nabla^2\rho_{\max(f)}$ is the local maximum value of $\nabla^2\rho$ at the front side of the Si-X bond. In principle, if this difference is large, back-side attack is preferred. In the case of $S_N2(C)$ reactions, the different substituents play a leading role in deciding which way the nucleophilic attack will proceed, because carbon does not have a large charge and does not have as large an attracting power as Si. Furthermore, the entering nucleophile always chooses to attack the deeper hole even though, the difference between the depths of the holes is quite small. Thus, back-side attack is always observed for $S_N2(C)$ reactions. Hence, the value $\Delta(\nabla^2\rho_{\max})$ does not relate to the ratio of front- and back-side attack in $S_N2(C)$ reactions. However, this number seems related to the ratio of front- and back-side attack in $S_N2(Si)$ reactions. From Table 5.4.1, the preference for back-side attack increases in the order $H < CCH < \underline{CN}$, $PH_2 < NH_2$, $\underline{NC} < OH$, OOH , $F < SH < Cl$. The experimentally observed order is $H < OR < F$, $SR < Cl$.^{82b,c} Therefore, it suggests that although the difference in $\nabla^2\rho$ between front and back side can not be revealed by VSCC in SiH_3X , the difference in the extent of charge depletion still exists. Thus, point by point calculations were carried out. The results for molecules SiH_3F and SiH_3Cl are provided in Table 5.4.3. The points were selected both at front and back side of X (i.e. opposite to Si-H and Si-X bond) with the distance to Si within the range 1.76 ± 0.5 a.u.. This radius was chosen since in CH_3X , the calculated extrema in VSCC of carbon occur at distances about 1.00 a.u. (see Table 5.4.1) which is very close to the radius of the outermost minimum of a free carbon atom (0.942 a.u.). Thus

Table 5.4.3 ρ and $\nabla^2\rho$ values at selected points in SiH_3F and SiH_3Cl .

SiH_3X	Point opposite to Si-H			Point opposite to Si-X			$\Delta(\nabla^2\rho)^d$
	r^a	ρ^b	$\nabla^2\rho^c$	r	ρ	$\nabla^2\rho$	
SiH_3F	1.259	0.063	1.083	1.259	0.061	1.102	0.019
	1.516	0.036	0.223	1.516	0.035	0.236	0.014
	1.753	0.027	0.088	1.753	0.025	0.095	0.007
	2.004	0.020	0.055	2.004	0.019	0.056	0.001
	2.247	0.015	0.040	2.247	0.013	0.039	-0.001
SiH_3Cl	1.245	0.067	1.171	1.245	0.065	1.191	0.020
	1.515	0.039	0.208	1.515	0.036	0.227	0.018
	1.767	0.029	0.071	1.767	0.026	0.084	0.013
	1.991	0.023	0.046	1.991	0.020	0.053	0.007
	2.241	0.017	0.037	2.241	0.014	0.038	0.001

^a The distance to Si (a.u.).

^b The ρ value at the point (a.u.).

^c The $\nabla^2\rho$ value at the point (a.u.).

^d The difference in $\nabla^2\rho$ values between points at back and at front.

the outermost minimum of a free Si atom (1.76 a.u. see Table 5.2.1) is used here. The data in Table 5.4.3 indicate that indeed there are differences in charge density and $\nabla^2\rho$ values at front and back side of molecules SiH_3F and SiH_3Cl . Furthermore, as observed in CH_3X , the back side has a small charge density and larger positive $\nabla^2\rho$ values. Moreover, the difference is larger in SiH_3Cl than in SiH_3F . Therefore, the difference in the extent of charge depletion at front and back side seems to be the reason for the different ratio of front- and back-side attacks.

In summary, the difference between $\text{S}_{\text{N}}2(\text{C})$ and $\text{S}_{\text{N}}2(\text{Si})$ reactions is mainly caused by the different electronegativities, polarizabilities and bonding characteristics of carbon and silicon. Gronert *et al.*⁸³ have recently reached a similar conclusion. Silicon forms ionic dominated bonds and it possesses a large positive charge in molecules. This enables $\text{S}_{\text{N}}2(\text{Si})$ reactions to proceed via both the retention and inversion processes. Moreover, the predominantly ionic bonds make the pentacoordinated silicon stable. Thus, instead of having a transition state, the reaction has a stable pentacoordinated intermediate which makes the reaction much faster. Hence, electronegativity and bonding character are important factors which make the chemistry of first-row elements different from that of the second-row elements. The observed stereochemistry of $\text{S}_{\text{N}}2(\text{Si})$ reactions is apparently related to the extent of charge depletion in different regions of space. If other conditions are the same, large differences in charge depletion between front and back side regions will result in an inversion dominated process. Otherwise, a retention dominated reaction process will be favoured.

Conclusions

Properties of the electronic charge distribution provide valuable insight into chemical problems. The integrated charges obtained from the molecular structure theory can be used to study the electronic structure of the transition state. The results indicate that the assumption that the reactant and product make the same contribution to the transition state wavefunction does not bear out for asymmetric reactions. The contributions of reactant and product to the TS are related to the type of reaction and to the exothermicity of the reaction. An exothermic reaction has an early TS, and the reactant contribution to the TS is larger than that of the product. Nevertheless, in some reactions, valence-bond configurations $N^{\cdot-} R \cdots X$ and $N \cdots R X^{\cdot-}$ (which are constituents of the reactant and product wavefunctions, respectively) make very similar contributions to the TS wavefunction. Therefore, in these reactions, the entering nucleophile and leaving group have equal charges at the TS.

The charge development on a leaving group (or entering nucleophile) is related not only to the exothermicity of the reaction but also to the electronegativity of X (or N) and to the contributions of ψ_3 or ψ_4 to the TS. If the electronegativities are equal and the contributions of ψ_3 or ψ_4 to the TS are equal, then the charge development on X (or N) correlates linearly with the exothermicity of the reaction.

The height of intrinsic barriers of symmetric reactions is affected by the type of the C-X bonding, the electronic structure of the TS and

the electronegativity of X. An *sp* hybridized X group leads to a relatively higher barrier. A large contribution from ψ_3 results in a lower barrier. A highly electronegative X yields a lower barrier.

For the S_N2 (C) reactions reported in this thesis, the rate-equilibrium relationship is observed when the reactions belong to the same type of reaction (as classified in section 4.2) and the α parameter appears to correlate with the properly defined geometry parameter R_α .

The Laplacian of the charge density study reveals that the differences in S_N2 (C) and S_N2 (Si) reaction processes are mainly caused by the different electronegativities, polarizabilities and bonding characteristics of carbon and silicon. The large positively charged Si can attract a nucleophile from all directions. The stereochemistry of silicon appears to correlate with the extent of charge depletion in various regions of space.

Appendices

Optimized Structures and Energies of Various Species

Energies are in atomic units, bond lengths are in angstroms and angles are in degrees. Unless specified otherwise, the basis sets are 6-31++G** except for the three methyl hydrogens for which the 6-31G basis sets is used.

1 Ions

Geometry parameters are defined in scheme 1.



Scheme 1

1.1 At the HF and MP2' levels.

X^-	-EHF	-EUMP2	r_1	β	r_2
H	0.48707	0.50363			
F	99.41859	99.62607			
Cl	459.53966	459.68147			
CN	92.31487	92.60851	1.1616		

1.1 (continued)

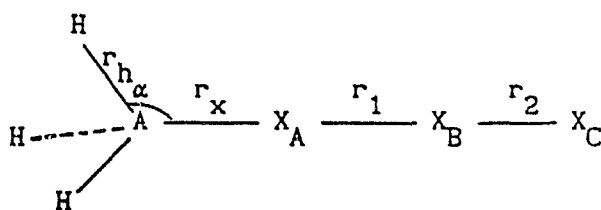
X^-	-EHF	-EUMP2	r_1	β	r_2
OH	75.38419	75.60481	0.9481		
SH	398.11122	398.25287	1.3377		
CCH	76.21247	76.48269	1.2331	180.0	1.0604
NH ₂	55.52768	55.73527	1.0161	103.489	
PH ₂	341.85785		1.4250	93.596	
OOH	150.16502		1.4689	101.804	0.9461

1.2 At the MP2 level.

X^-	-EUMP2	r_1	β	r_2
CN	92.61141	1.2007		
OH	75.60530	0.9705		
SH	398.25287	1.3392		
CCH	76.48399	1.2616	180.000	1.0702
NH ₂	55.73553	1.0294	102.969	
PH ₂	341.99299	1.4222	92.101	

2 Molecule CH₃X and SiH₃X2.1 C_{3v} symmetry.

Geometry parameters are defined in scheme 2.1.



Scheme 2.1

2.1.1 At the HF and MP2' levels.

AH_3X	$-\text{E}^{\text{a}}$	r_{x}	α	r_{h}	r_1	r_2
$\text{CH}_3\text{H}^{\text{b}}$	40.19567 40.33849	1.0840	109.471	1.0840		
$\text{CH}_3\text{H}^{\text{c}}$	40.20217 40.37141	1.0840	109.471	1.0840		
CH_3F	139.04423 139.35979	1.3714	108.493	1.0807		
CH_3Cl	499.09416 499.37238	1.7855	108.421	1.0779		
CH_3CN	131.93117 132.35444	1.4690	109.748	1.0821	1.1356	
CH_3NC	131.90083 132.31441	1.4233	109.437	1.0808	1.1521	
CH_3CCH	115.87154 116.26951	1.4689	110.510	1.0837	1.1900	1.0568
$\text{SiH}_3\text{H}^{\text{b}}$	291.22630	1.4746	109.471	1.4746		
SiH_3F	390.15539	1.6048	108.201	1.4681		
SiH_3Cl	750.18467	2.0690	108.227	1.4668		

^a The RHF energy is followed by the MP2' energy.

^b Basis set 6-31+G*.

^c Basis set 6-31++G** for all the atoms including the three methyl hydrogens. Calculations done at the HF/6-31++G**//HF/6-31+G* and MP2/6-31++G**//HF/6-31+G* levels.

2.1.2 At the MP2 level.

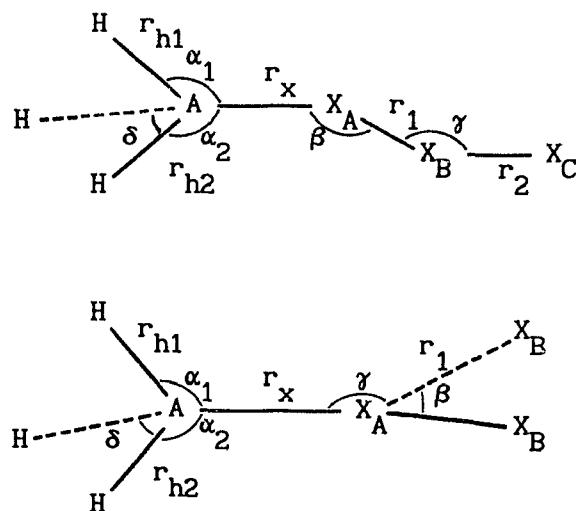
CH_3X	-EUMP2	r_x	α	r_h	r_1	r_2
CH_3H^b	40.33861	1.0905	109.471	1.0905		
CH_3H^c	40.37134	1.0905	109.471	1.0906		
CH_3F	139.36074	1.4056	108.104	1.0900		
CH_3Cl	499.37263	1.7787	108.880	1.0885		
CH_3CN	132.35876	1.4621	110.030	1.0919	1.1795	
CH_3NC	132.31695	1.4254	109.253	1.0907	1.1862	
CH_3CCH	116.27158	1.4623	110.735	1.0935	1.2211	1.0625

^b See footnote b of appendix 2.1.1.

^c Calculation done at the MP2/6-31++G**//MP2/6-31+G* level.

2.2 C_s symmetry.

Geometry parameters are defined in scheme 2.2.



Scheme 2.2

2.2.1 At the HF and MP2' level.

CH ₃ OH	-EHF	115.04785	r _x	1.4010	α ₁	107.058	r ₁	0.9423
	-EUMP2	115.37632	r _{h1}	1.0807	α ₂	111.717	β	110.537
			r _{h2}	1.0865	δ	109.010		
CH ₃ SH	-EHF	437.70525	r _x	1.8181	α ₁	106.800	r ₁	1.3278
	-EUMP2	437.98302	r _{h1}	1.0816	α ₂	111.244	β	97.912
			r _{h2}	1.0811	δ	109.950		
CH ₃ COH	-EHF	189.80897	r _x	1.3976	α ₁	105.297	r ₁	1.4002
	-EUMP2	190.32283	r _{h1}	1.0814	α ₂	110.550	β	105.962
			r _{h2}	1.0834	δ	110.048	r ₂	0.9455
							γ	101.519
CH ₃ NH ₂	-EHF	95.22184	r _x	1.4525	α ₁	114.511	r ₁	0.9997
	-EUMP2	95.54337	r _{h1}	1.0901	α ₂	109.239	β	107.840
			r _{h2}	1.0838	δ	107.440	γ	111.629
CH ₃ PH ₂	-EHF	381.49167	r _x	1.8606	α ₁	113.320	r ₁	1.4059
	-EUMP2	381.76001	r _{h1}	1.0830	α ₂	109.203	β	95.280
			r _{h2}	1.0846	δ	107.555	γ	98.759
SiH ₃ OH	-EHF	366.14285	r _x	1.6491	α ₁	106.748	r ₁	0.9413
			r _{h1}	1.4676	α ₂	111.036	β	121.619
			r _{h2}	1.4759	δ	107.989		

SiH ₃ SH	-EHF	688.77627	r _x	2.1525	α ₁	105.304	r ₁	1.3293
			r _{h1}	1.4693	α ₂	110.960	β	97.460
			r _{h2}	1.4716	δ	108.856		

2.2.2 At the MP2 level.

CH ₃ OH	-EUMP2	115.37746	r _x	1.4285	α ₁	106.123	r ₁	0.9636
			r _{h1}	1.0896	α ₂	111.721	β	108.683
			r _{h2}	1.0957	δ	109.344		

CH ₃ SH	-EUMP2	437.98327	r _x	1.8150	α ₁	106.754	r ₁	1.3301
			r _{h1}	1.0909	α ₂	111.599	β	96.607
			r _{h2}	1.0907	δ	109.878		

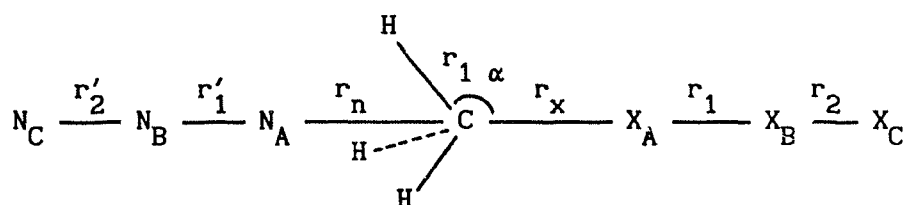
CH ₃ NH ₂	-EUMP2	95.54386	r _x	1.4636	α ₁	115.009	r ₁	1.0120
			r _{h1}	1.0992	α ₂	108.686	β	107.249
			r _{h2}	1.0923	δ	107.670	γ	110.956

CH ₃ PH ₂	-EUMP2	381.76020	r _x	1.8575	α ₁	113.805	r ₁	1.4067
			r _{h1}	1.0914	α ₂	109.011	β	94.877
			r _{h2}	1.0928	δ	107.493	γ	97.909

3 Ion-molecule Complexes

3.1 C_{3v} symmetry

Geometry parameters are defined in scheme 3.1



Scheme 3.1

3.1.1 At the HF and MP2' levels.

$\text{H}^- \cdots \text{RH}$	-EHF	40.68460	r_n	5.1677	α 110.031
	-EUMP2	40.85093			
				r_x	
				r_h	
$\text{H}^- \cdots \text{RF}$	-EHF	139.54327	r_n	3.2381	α 108.433
	-EUMP2	139.87739			
				r_x	
				r_h	
$\text{F}^- \cdots \text{RH}$	-EHF	139.61744	r_n	3.3360	α 110.890
	-EUMP2	139.97546			
				r_x	
				r_h	
$\text{H}^- \cdots \text{RC1}$	-EHF	499.59500	r_n	3.0855	α 107.861
	-EUMP2	499.89068			
				r_x	
				r_h	

$\text{Cl}^- \cdots \text{RH}$	-EHF	499.73743	r_n	4.4606	α	110.217	
	-EUMP2	500.02951	r_x	1.0875			
			r_h	1.0827			
$\text{H}^- \cdots \text{RCN}$	-EHF	132.43620	r_n	3.2205	α	110.860	r_1 1.1384
	-EUMP2	132.87767	r_x	1.4747			
			r_h	1.0798			
$\text{NC}^- \cdots \text{RH}$	-EHF	132.51265	r_n	4.4633	α	110.155	r'_1 1.1615
	-EUMP2	132.95637	r_x	1.0872			
			r_h	1.0828			
$\text{H}^- \cdots \text{RNC}$	-EHF	132.40505	r_n	3.1589	α	109.837	r_1 1.1497
	-EUMP2	132.83926	r_x	1.4447			
			r_h	1.0770			
$\text{CN}^- \cdots \text{RH}$	-EHF	132.51279	r_n	3.8778	α	110.336	r'_1 1.1615
	-EUMP2	132.95673	r_x	1.0879			
			r_h	1.0825			
$\text{H}^- \cdots \text{RCCH}$	-EHF	116.36573	r_n	3.5596	α	111.324	r_1 1.1933
	-EUMP2	116.78225	r_x	1.4734			r_2 1.0559
			r_h	1.0816			

HCC $\bar{\cdot}\cdot\cdot$ RH	-EHF 116.41029	r_n 4.3898	α 110.260	r'_1 1.2329
	-EUMP2 116.83067	r_x 1.0877		r'_2 1.0603
		r_h 1.0827		
F $\bar{\cdot}\cdot\cdot$ RF	-EHF 238.48328	r_n 2.6739	α 108.125	
	-EUMP2 239.00804	r_x 1.4155		
		r_h 1.0739		
F $\bar{\cdot}\cdot\cdot$ RC1	-EHF 598.53587	r_n 2.5851	α 107.034	
	-EUMP2 599.02053	r_x 1.8628		
		r_h 1.0700		
Cl $\bar{\cdot}\cdot\cdot$ RF	-EHF 598.59670	r_n 3.4224	α 108.381	
	-EUMP2 599.05622	r_x 1.3982		
		r_h 1.0765		
F $\bar{\cdot}\cdot\cdot$ RCN	-EHF 231.37717	r_n 2.7222	α 111.317	r_1 1.1395
	-EUMP2 232.00838	r_x 1.4769		
		r_h 1.0785		
NC $\bar{\cdot}\cdot\cdot$ RF	-EHF 231.37149	r_n 3.2880	α 108.409	r'_1 1.1604
	-EUMP2 231.98251	r_x 1.3971		
		r_h 1.0766		

$\text{F}^{\cdot\cdot\cdot}\text{RNC}$	-EHF	231.34643	r_n	2.6641	α	109.833	r_1	1.1493
	-EUMP2	231.97104	r_x	1.4547				
			r_h	1.0748				
$\text{CN}^{\cdot\cdot\cdot}\text{RF}$	-EHF	231.37287	r_n	3.0348	α	108.375	r_1	1.1614
	-EUMP2	231.98359	r_x	1.3994				
			r_h	1.0762				
$\text{F}^{\cdot\cdot\cdot}\text{RCCH}$	-EHF	215.30377	r_n	2.8665	α	111.885	r_1	1.1949
			r_x	1.4755			r_2	1.0557
			r_h	1.0801				
$\text{HCC}^{\cdot\cdot\cdot}\text{RF}$	-EHF	215.27066	r_n	3.2690	α	108.380	r'_1	1.2313
			r_x	1.4013			r'_2	1.0601
			r_h	1.0761				
$\text{Cl}^{\cdot\cdot\cdot}\text{RCl}$	-EHF	958.64797	r_n	3.3670	α	107.965		
	-EUMP2	959.06898	r_x	1.8244				
			r_h	1.0735				
$\text{Cl}^{\cdot\cdot\cdot}\text{RCN}$	-EHF	591.48953	r_n	3.4190	α	110.731	r_1	1.1382
	-EUMP2	592.05656	r_x	1.4738				
			r_h	1.0798				

$\text{NC}^{\cdot\cdot\cdot}\text{RC1}$	-EHF	591.42242	r_n	3.2442	α	107.987	r_1	1.1602
	-EUMP2	591.99483						
			r_x	1.8233				
			r_h	1.0734				

$\text{NC}^{\cdot\cdot\cdot}\text{RCN}$	-EHF	224.26352	r_n	3.3338	α	110.724	r_1	1.1381
	-EUMP2	224.98142						
			r_x	1.4340			r'_1	1.1602
			r_h	1.0797				

$\text{CN}^{\cdot\cdot\cdot}\text{RNC}$	-EHF	224.23435	r_n	3.0123	α	109.762	r_1	1.1497
			r_x	1.4439			r'_1	1.1615
			r_h	1.0766				

$\text{HCC}^{\cdot\cdot\cdot}\text{RCCH}$	-EHF	192.09257	r_n	3.5276	α	111.411	r_1	1.1935
			r_x	1.4735			r_2	1.0559
			r_h	1.0812			r'_1	1.2319
							r'_2	1.0602

3.1.2 At the MP2 level.

$\text{H}^{\cdot\cdot\cdot}\text{RH}$	-EUMP2	40.85121	r_n	4.2644	α	110.386		
			r_x	1.0889				
			r_h	1.0839				

$\text{H}^{\cdot\cdot\cdot}\text{RF}$	-EUMP2	139.87862	r_n	2.9963	α	108.120		
			r_x	1.4407				
			r_h	1.0859				

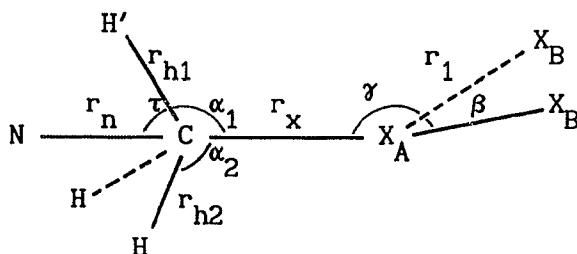
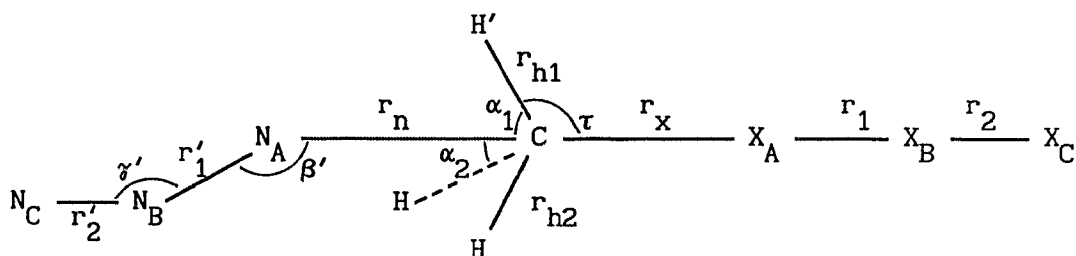
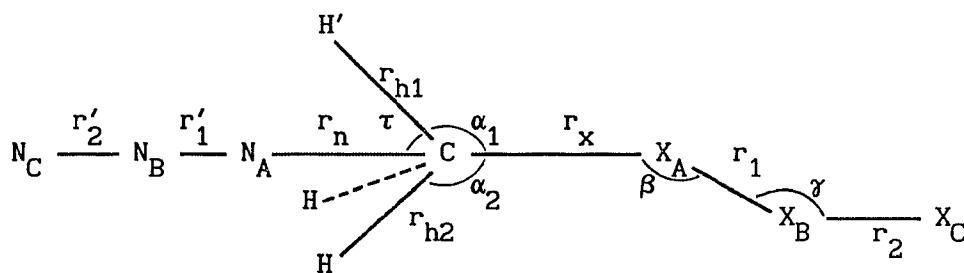
$\text{F}^{\cdot\cdot}\cdots\text{RH}$	-EUMP2 139.97559	r_n 3.2351	α 111.218	
		r_x 1.0912		
		r_h 1.0886		
$\text{H}^{\cdot\cdot}\cdots\text{RC1}$	-EUMP2 499.89122	r_n 2.9430	α 108.878	
		r_x 1.8199		
		r_h 1.0846		
$\text{Cl}^{\cdot\cdot}\cdots\text{RH}$	-EUMP2 500.02978	r_n 4.0175	α 110.530	
		r_x 1.0893		
		r_h 1.0891		
$\text{H}^{\cdot\cdot}\cdots\text{RCN}$	-EUMP2 132.88198	r_n 3.0863	α 111.622	r_1 1.1813
		r_x 1.4646		
		r_h 1.0902		
$\text{NC}^{\cdot\cdot}\cdots\text{RH}$	-EUMP2 132.95948	r_n 4.0347	α 110.436	r'_1 1.2005
		r_x 1.0889		
		r_h 1.0892		
$\text{H}^{\cdot\cdot}\cdots\text{RNC}$	-EUMP2 132.84240	r_n 2.9579	α 110.183	r_1 1.1855
		r_x 1.4444		
		r_h 1.0874		

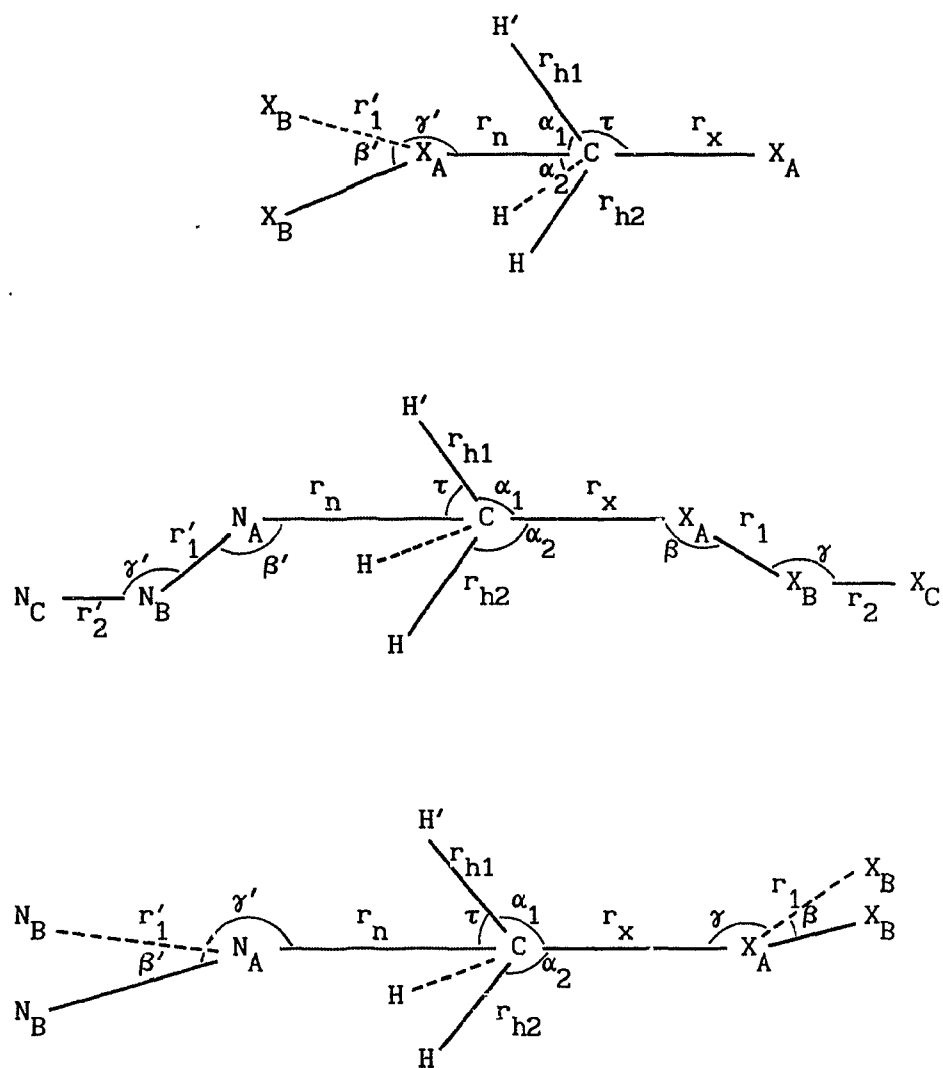
$\text{CN}^{\cdot\cdot}\cdots\text{RH}$	-EUMP2 132.95985	r_n 3.5918 r_x 1.0893 r_h 1.0891	α 110.586	r'_1 1.2006
$\text{H}^{\cdot\cdot}\cdots\text{RCCH}$	-EUMP2 116.78444	r_n 3.3723 r_x 1.4646 r_h 1.0917	α 111.991	r_1 1.2243 r_2 1.0617
$\text{HCC}^{\cdot\cdot}\cdots\text{RH}$	-EUMP2 116.83217	r_n 4.0048 r_x 1.0897 r_h 1.0890	α 110.619	r'_1 1.2616 r'_2 1.0707
$\text{F}^{\cdot\cdot}\cdots\text{RF}$	-EUMP2 239.00898	r_n 2.6266 r_x 1.4542 r_h 1.0835	α 107.728	
$\text{F}^{\cdot\cdot}\cdots\text{RCI}$	-EUMP2 599.02110	r_n 2.6154 r_x 1.8309 r_h 1.0822	α 108.542	
$\text{Cl}^{\cdot\cdot}\cdots\text{RF}$	-EUMP2 599.05741	r_n 3.2513 r_x 1.4366 r_h 1.0857	α 108.022	

$\text{Cl} \cdots \text{RC1}$ -EUMP2 959.06949 r_n 3.2664 α 108.888
 r_x 1.8085
 r_h 1.0845

3.2 C_s symmetry

Geometry parameters are defined in scheme 3.2





dihedral angle D ($H'CX_AH$)

Scheme 3.2

3.2.1 Results at the HF and MP2' levels.

$H^+ \cdots ROH$	-EHF	115.54084	r_n	3.6187	α_1	107.474	r_1	0.9416
	-EUMP2	115.88780						
			r_x	1.4200	α_2	111.704	β	109.208
			r_{h1}	1.0780	D	118.840		

			r_{h2} 1.0824	τ 72.526 ^a		
$HO\ddot{O}\cdots RH$	-EHF 115.58352 -EUMP2 115.95505		r_n 3.2754	α_1 69.385	r'_1 0.9476	
			r_x 1.0910	α_2 68.830	β' 179.338	
			r_{h1} 1.0817	D 119.885		
			r_{h2} 1.0817	τ 110.265		
$H\ddot{O}\cdots RSH$	-EHF 438.20019 -EUMP2 438.49614		r_n 3.4738	α_1 107.316	r_1 1.3283	
			r_x 1.8317	α_2 111.478	β 98.510	
			r_{h1} 1.0790	D 118.549		
			r_{h2} 1.0775	τ 72.684 ^a		
$HS\ddot{O}\cdots RH$	-EHF 438.30909 -EUMP2 438.60116		r_n 4.2546	α_1 68.827	r'_1 1.3372	
			r_x 1.0881	α_2 70.284	β' 171.191	
			r_{h1} 1.0828	D 120.295		
			r_{h2} 1.0827	τ 110.187		
$H\ddot{O}\cdots ROOH$	-EHF 190.30217 -EUMP2 190.83463		r_n 3.4716	α_1 105.399	r_1 1.4032	
			r_x 1.4162	α_2 110.802	β 106.599	
			r_{h1} 1.0788	D 118.876	r_2 0.9440	
			r_{h2} 1.0795	τ 74.601 ^a	γ 101.085	
$HOO\ddot{O}\cdots RH$	-EHF 190.36408 -EUMP2 190.91225		r_n 3.5510	α_1 69.710	r'_1 1.4691	
			r_x 1.0901	α_2 69.042	β' 73.856	
			r_{h1} 1.0827	D 120.153	r'_2 0.9415	
			r_{h2} 1.0817	τ 110.290	γ' 101.790	

$\text{H}^{\cdot}\cdots\text{RNH}_2$	-EHF	95.71127	r_n	4.0703	α_1	114.424	r_1	1.0008
	-EUMP2	96.05082	r_x	1.4642	α_2	109.640	β	107.106
			r_{h1}	1.0859	D	121.332	γ	110.692
			r_{h2}	1.0816	τ	65.576 ^a		
$\text{H}_2\text{N}^{\cdot}\cdots\text{RH}$	-EHF	95.72608	r_n	3.7918	α_1	69.167	r'_1	1.0160
	-EUMP2	96.08431	r_x	1.0897	α_2	69.316	β'	103.321
			r_{h1}	1.0819	D	120.112	γ'	128.339
			r_{h2}	1.0821	τ	110.833 ^a		
$\text{H}^{\cdot}\cdots\text{RPH}_2$	-EHF	381.98313	r_n	3.8360	α_1	113.960	r_1	1.4085
	-EUMP2	382.26959	r_x	1.8545	α_2	109.999	β	94.864
			r_{h1}	1.0805	D	121.353	γ	99.832
			r_{h2}	1.0828	τ	66.040 ^a		
$\text{H}_2\text{P}^{\cdot}\cdots\text{RH}$	-EHF	382.05552	r_n	4.8998	α_1	66.414	r'_1	1.4249
	-EUMP2	382.34093	r_x	1.0872	α_2	71.744	β'	94.127
			r_{h1}	1.0824	D	121.092	γ'	132.924
			r_{h2}	1.0831	τ	110.118		
$\text{F}^{\cdot}\cdots\text{ROH}$	-EHF	214.47797	r_n	2.8695	α_1	107.604	r_1	0.9414
	-EUMP2	215.01601	r_x	1.4311	α_2	111.733	β	108.870
			r_{h1}	1.0760	D	118.859		
			r_{h2}	1.0799	τ	72.396 ^a		

$\text{HO}^{\cdot-}\cdots\text{RF}$	-EHF 214.44956	r_n 2.7378	α_1 66.940	r'_1 0.9455
	-EUMP2 214.98779	r_x 1.4148	α_2 74.195	β' 168.997
		r_{h1} 1.0737	D 121.172	
		r_{h2} 1.0744	τ 117.526	
$\text{F}^{\cdot-}\cdots\text{RSH}$	-EHF 537.13813	r_n 2.8038	α_1 107.450	r_1 1.3288
	-EUMP2 537.62446	r_x 1.8419	α_2 111.541	β 98.851
		r_{h1} 1.0771	D 118.563	
		r_{h2} 1.0752	τ 72.550 ^a	
$\text{HS}^{\cdot-}\cdots\text{RF}$	-EHF 537.16736	r_n 3.5838	α_1 66.913	r_1 1.3362
	-EUMP2 537.62739	r_x 1.3972	α_2 74.043	β' 126.68
		r_{h1} 1.0776	D 121.167	
		r_{h2} 1.0766	τ 108.332	
$\text{F}^{\cdot-}\cdots\text{RNH}_2$	-EHF 194.64641	r_n 3.0425	α_1 114.655	r_1 1.0015
	-EUMP2 195.17741	r_x 1.4723	α_2 110.906	β 106.669
		r_{h1} 1.0832	D 121.324	γ 110.415
		r_{h2} 1.0798	τ 65.345 ^a	
$\text{H}_2\text{N}^{\cdot-}\cdots\text{RF}$	-EHF 194.59114	r_n 2.9533	α_1 71.627	r'_1 1.0144
	-EUMP2 195.11701	r_x 1.4135	α_2 71.787	β' 103.337
		r_{h1} 1.0738	D 120.234	γ' 128.327
		r_{h2} 1.0746	τ 108.373 ^a	
$\text{F}^{\cdot-}\cdots\text{RPH}_2$	-EHF 480.91917	r_n 2.9729	α_1 114.752	r_1 1.4102
	-EUMP2 481.39677			

			r_x	1.8538	α_2	110.528	β	94.699
			r_{h1}	1.0787	D	121.432	γ	100.452
			r_{h2}	1.0814	τ	65.248		
$H_2P^{\cdot\cdot} \cdots RF$	-EHF	480.91292	r_n	3.7301	α_1	69.440	r'_1	1.4223
	-EUMP2	481.36621	r_x	1.3938	α_2	72.692	β'	94.127
			r_{h1}	1.0767	D	120.724	γ'	132.924
			r_{h2}	1.0775	τ	108.507		
$Cl^{\cdot\cdot} \cdots ROH$	-EHF	574.59432	r_n	3.6519	α_1	107.458	r_1	0.9416
	-EUMP2	575.06685	r_x	1.4205	α_2	111.687	β	109.212
			r_{h1}	1.0778	D	118.842		
			r_{h2}	1.0821	τ	72.542 ^a		
$HO^{\cdot\cdot} \cdots RC1$	-EHF	574.50252	r_n	2.6562	α_1	70.404	r'_1	0.9452
	-EUMP2	575.00058	r_x	1.8567	α_2	73.735	β'	183.910
			r_{h1}	1.0705	D	120.517		
			r_{h2}	1.0706	τ	111.642		
$Cl^{\cdot\cdot} \cdots RSH$	-EHF	897.25355	r_n	3.5868	α_1	107.290	r_1	1.3282
	-EUMP2	897.67493	r_x	1.8300	α_2	111.487	β	98.524
			r_{h1}	1.0790	D	118.571		
			r_{h2}	1.0774	τ	72.710 ^a		
$HS^{\cdot\cdot} \cdots RC1$	-EHF	897.21859	r_n	3.5188	α_1	67.336	r'	1.3356
	-EUMP2	897.64052	r_x	1.8210	α_2	74.333	β'	126.793

			r_{h1}	1.0742	D	121.155	
			r_{h2}	1.0738	τ	107.943	
$\text{NC}^-\cdots\text{ROH}$	-EHF	207.36924	r_n	3.5385	α_1	107.470	r_1 0.9416
	-EUMP2	207.99313	r_x	1.4192	α_2	111.690	β 109.283
			r_{h1}	1.0779	D	118.835	r'_1 1.1609
			r_{h2}	1.0823	τ	72.530 ^a	
$\text{HO}^-\cdots\text{RCN}$	-EHF	207.34458	r_n	2.7431	α_1	67.276	r_1 1.1397
	-EUMP2	207.98963	r_x	1.4754	α_2	69.186	r'_1 0.9453
			r_{h1}	1.0788	D	120.393	β' 180.134
			r_{h2}	1.0788	τ	113.887	
$\text{NC}^-\cdots\text{RSH}$	-EHF	530.02812	r_n	3.4983	α_1	107.324	r_1 1.3282
	-EUMP2	530.60096	r_x	1.8297	α_2	111.468	β 98.474
			r_{h1}	1.0789	D	118.561	r'_1 1.1608
			r_{h2}	1.0774	τ	72.676 ^a	
$\text{HS}^-\cdots\text{RCN}$	-EHF	530.06043	r_n	3.4139	α_1	69.361	r_1 1.1381
	-EUMP2	530.62780	r_x	1.4724	α_2	69.526	r'_1 1.3342
			r_{h1}	1.0807	D	120.102	β' 168.097
			r_{h2}	1.0803	τ	110.867	
$\text{HO}^-\cdots\text{ROH}$	-EHF	190.44420	r_n	2.9050	α_1	107.617	r_1 0.9415
	-EUMP2	190.99583	r_x	1.4325	α_2	111.738	β 108.812
			r_{h1}	1.0758	D	118.828	r'_1 0.9464

			r_{h2} 1.0800	τ 72.383 ^a	β' 170.290
$HO^{\cdot-} \cdots RSH$	-EHF 513.10501	r_n 2.8285	α_1 107.447	r_1 1.3289	
	-EUMP2 513.60500	r_x 1.8407	α_2 111.640	β 98.911	
		r_{h1} 1.0773	D 118.539	r'_1 0.9462	
		r_{h2} 1.0754	τ 72.553 ^a	β' 178.884	
$HS^{\cdot-} \cdots ROH$	-EHF 513.16543	r_n 3.6814	α_1 107.313	r_1 0.9417	
	-EUMP2 513.63779	r_x 1.4188	α_2 111.634	β 109.187	
		r_{h1} 1.0784	D 118.844	r'_1 1.3359	
		r_{h2} 1.0825	τ 72.687 ^a	β' 170.382	
$HS^{\cdot-} \cdots RS^{\cdot}$	-EHF 835.82485	r_n 3.5748	α_1 107.285	r_1 1.3282	
	-EUMP2 836.24639	r_x 1.8285	α_2 111.302	β 98.474	
		r_{h1} 1.0791	D 118.495	r'_1 1.3356	
		r_{h2} 1.0781	τ 72.715 ^a	β' 168.552	
$HOO^{\cdot-} \cdots ROOH$	-EHF 339.98552	r_n 2.9723	α_1 104.835	r_1 1.4045	
		r_x 1.4251	α_2 110.954	β 106.955	
		r_{h1} 1.0783	D 119.034	r_2 0.9436	
		r_{h2} 1.0775	τ 75.165 ^a	γ 100.982	
				r'_1 1.4652	
				β' 83.344	
				r'_2 0.9412	
				γ' 101.967	

$\text{H}_2\text{N}^{\cdot\cdot}\cdots\text{RNH}_2$	-EHF	150.75471	r_n	3.3838	α_1	114.731	r_1	1.0014
	-EUMP2	151.28627	r_x	1.4716	α_2	109.919	β	106.710
			r_{h1}	1.0832	D	121.476	γ	110.339
			r_{h2}	1.0802	τ	65.269 ^a	r'_1	1.0156
							β'	103.241
							γ'	128.378
$\text{H}_2\text{P}^{\cdot\cdot}\cdots\text{RPH}_2$	-EHF	723.35386	r_n	4.1242	α_1	113.971	r_1	1.4083
			r_x	1.8542	α_2	109.798	β	94.940
			r_{h1}	1.0807	D	121.495	γ	99.733
			r_{h2}	1.0831	τ	66.029 ^a	r'_1	1.4239
							β'	93.756
							γ'	133.121

^a The angle is fixed so that the back-side attack is studied.

3.2.2 At the MP2 level.

$\text{H}^{\cdot\cdot}\cdots\text{ROH}$	-EUMP2	115.88924	r_n	3.3142	α_1	106.485	r_1	0.9632
			r_x	1.4524	α_2	111.840	β	107.114
			r_{h1}	1.0867	D	118.623		
			r_{h2}	1.0911	τ	73.515 ^a		
$\text{HO}^{\cdot\cdot}\cdots\text{RH}$	-EUMP2	115.95583	r_n	3.0966	α_1	69.160	r'_1	0.9706
			r_x	1.0919	α_2	68.331	β'	179.326
			r_{h1}	1.0887	D	119.821		
			r_{h2}	1.0886	τ	110.302		

$\text{H}^{\cdot-} \cdots \text{RSH}$	-EUMP2 438.49666	r_n	3.2350	α_1	107.675	r_1	1.3307
		r_x	1.8273	α_2	112.223	β	97.201
		r_{h1}	1.0887	D	118.354		
		r_{h2}	1.0876	τ	72.325 ^a		
$\text{HS}^{\cdot-} \cdots \text{RH}$	-EUMP2 438.60180	r_n	3.8328	α_1	69.748	r'_1	1.3390
		r_x	1.0895	α_2	69.387	β'	150.258
		r_{h1}	1.0897	D	119.991		
		r_{h2}	1.0890	τ	110.252 ^a		
$\text{H}^{\cdot-} \cdots \text{RNH}_2$	-EUMP2 96.05166	r_n	3.6158	α_1	115.104	r_1	1.0137
		r_x	1.4783	α_2	109.415	β	106.324
		r_{h1}	1.0942	D	121.513	γ	109.855
		r_{h2}	1.0899	τ	64.896 ^a		
$\text{H}_2\text{N}^{\cdot-} \cdots \text{RH}$	-EUMP2 96.08494	r_n	3.4112	α_1	68.452	r'_1	1.0300
		r_x	1.0916	α_2	68.860	β'	102.654
		r_{h1}	1.0884	D	120.277	γ'	128.672
		r_{h2}	1.0887	τ	111.548 ^a		
$\text{F}^{\cdot-} \cdots \text{ROH}$	-EUMP2 215.01723	r_n	2.8116	α_1	106.727	r_1	0.9631
		r_x	1.4619	α_2	111.838	β	106.856
		r_{h1}	1.0849	D	118.647		
		r_{h2}	1.0890	τ	73.273 ^a		
$\text{HO}^{\cdot-} \cdots \text{RF}$	-EUMP2 214.98943	r_n	2.6728	α_1	60.825	r'_1	0.9688

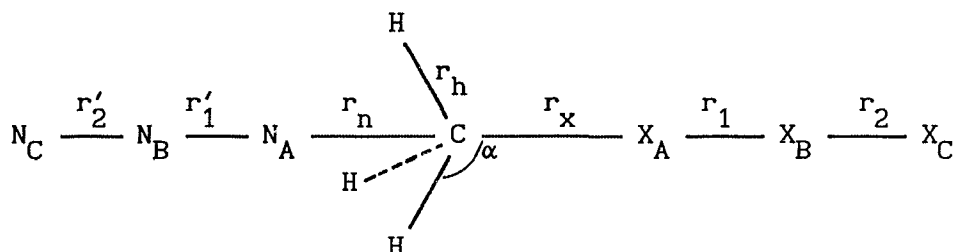
r_x	1.4524	α_2	77.941	β'	156.276
r_{h1}	1.0837	D	122.325		
r_{h2}	1.0845	τ	108.741		

^a The angle is fixed so that the back-side attack is studied.

4 Transition State

4.1 C_{3v} symmetry

Geometry parameters are defined in scheme 4.1



Scheme 4.1

4.1.1 Results at the HF and MP2' levels. The first column is the nucleophile N and the second column is the leaving group X.

H	H	-EHF	40.58401	r_n	1.6897	α	89.997
		-EUMP2	40.76137				
				r_x	1.6900		
				r_h	1.0613		
H	F	-EHF	139.51200	r_n	1.8742	α	94.353
		-EUMP2	139.86485				
				r_x	1.7640		
				r_h	1.0622		

H	Cl	-EHF 499.58875 -EUMF 499.88484	r_n 2.2353 r_x 2.0856 r_h 1.0644	α 100.048	
H	CN	-EHF 132.38192 -EUMP2 132.82921	r_n 1.9093 r_x 1.9960 r_h 1.0620	α 95.077	r_1 1.1506
H	NC	-EHF 132.37329 -EUMP2 132.81609	r_n 2.0038 r_x 1.8513 r_h 1.0618	α 96.502	r_1 1.1563
H	CCH	-EHF 116.29150 -EUMP2 116.71660	r_n 1.8463 r_x 2.0568 r_h 1.0510	α 93.456	r_1 1.2167 r_2 1.0585
F	F	-EHF 238.45374 -EUMP2 238.98797	r_n 1.8461 r_x 1.8460 r_h 1.0609	α 90.010	
F	Cl	-EHF 598.53111 -EUMP2 599.01096	r_n 2.1255 r_x 2.1332 r_h 1.0619	α 97.277	
F	CN	-EHF 231.32268 -EUMP2 231.94975	r_n 1.8816 r_x 2.0720	α 91.055	r_1 1.1519

				r_h	1.0615		
F	<u>NC</u>	-EHF -EUMP2	231.31748 231.94199	r_n	1.9503	α 93.2425	r_1 1.1564
				r_x	1.9029		
				r_h	1.0607		
F	CCH	-EHF -EUMP2	215.23069 215.83418	r_n	1.8399	α 89.300	r_1 1.2190
				r_x	2.1433		r_2 1.0588
				r_h	1.0610		
Cl	Cl	-EHF -EUMP2	958.62331 959.04024	r_n	2.3931	α 89.994	
				r_x	2.3937		
				r_h	1.0617		
Cl	<u>CN</u>	-EHF -EUMP2	591.40406 591.97314	r_n	2.2472	α 86.253	r_1 1.1539
				r_x	2.3180		
				r_h	1.0619		
<u>NC</u>	<u>CN</u>	-EHF -EUMP2	224.18955 224.90867	r_n	2.1356	α 90.000	r_1 1.1520
				r_x	2.1356		r'_1 1.1520
				r_h	1.0616		
<u>CN</u>	<u>NC</u>	-EHF	224.18311	r_n	2.0315	α 90.000	r_1 1.1581
				r_x	2.0315		r'_1 1.1581
				r_h	1.0608		

HCC	CCH	-EHF	192.00726	r_n	2.1454	α	90.00	r_1	1.2182
				r_x	2.1454			r_2	1.0589
				r_h	1.0605			r'_1	1.2182
								r'_2	1.0589

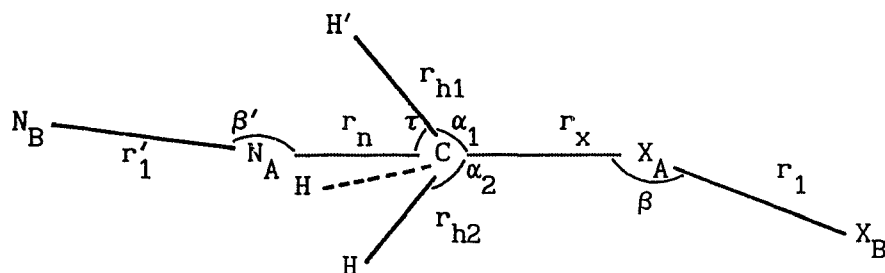
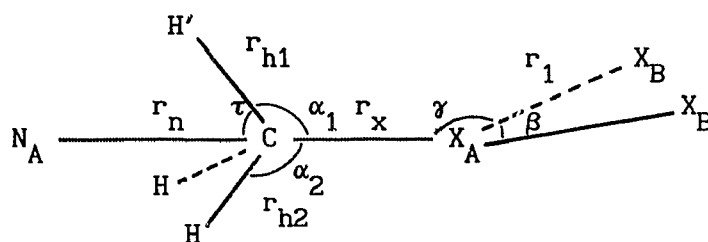
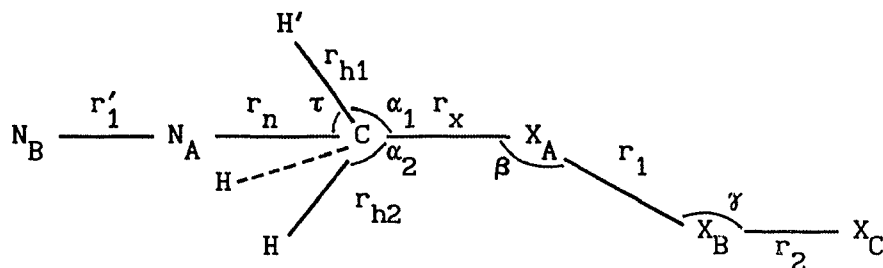
4.1.2 At the MP2 level.

H	H	-EUMP2	40.76328	r_n	1.589'	α	90.000		
				r_x	1.5891				
				r_h	1.0728				
H	F	-EUMP2	139.86439	r_n	1.9278	α	98.018		
				r_x	1.6955				
				r_h	1.0759				
H	Cl	-EUMP2	499.88623	r_n	2.1524	α	102.464		
				r_x	2.0266				
				r_h	1.0778				
H	<u>C</u> N	-EUMP2	132.83390	r_n	1.8454	α	96.559	r_1	1.1926
				r_x	1.9271				
				r_h	1.0741				
H	<u>N</u> C	-EUMP2	132.81974	r_n	1.9642	α	98.893	r_1	1.1936
				r_x	1.7743				
				r_h	1.0753				

H	CCH	-EUMP2 116.71942	r_n 1.7799	α 94.830	r_1 1.2467
			r_x 1.9824		r_2 1.0671
			r_h 1.0733		
F	F	-EUMP2 238.98838	r_n 1.8355	α 90.000	
			r_x 1.8355		
			r_h 1.0740		
F	Cl	-EUMP2 599.01137	r_n 2.0134	α 95.598	
			r_x 2.1419		
			r_h 1.0733		
F	CN	-EUMP2 231.95356	r_n 1.8290	α 89.473	r_1 1.1933
			r_x 2.0651		
			r_h 1.0742		
Cl	Cl	-EUMP2 959.04186	r_n 2.3158	α 90.001	
			r_x 2.3159		
			r_h 1.0724		

4.2 C_s symmetry.

Geometry parameters are defined in scheme 4.2



dihedral angle $D(H'CX_AH)$

Scheme 4.2

4.2.1 Results at the HF and MP2' levels.

H	OH	-EHF	115.48390	r_n	1.7905	α_1	89.930	r_1	0.9459
		-EUMP2	115.85461						
				r_x	1.8901	α_2	94.256	β	109.651
				r_{h1}	1.0617	D	119.637		
				r_{h2}	1.0620	τ	88.123		

H	SH	-EHF	438.17416	r_n	2.0292	α_1	96.058	r_1	1.3321
		-EUMP2	438.47462	r_x	2.2526	α_2	97.905	β	97.284
				r_{h1}	1.0639	D	119.534		
				r_{h2}	1.0626	τ	83.413		
H	OOH	-EHF	190.25718	r_n	1.8346	α_1	91.178	r_1	1.4289
		-EUMP2	190.80072	r_x	1.8346	α_2	94.638	β	104.699
				r_{h1}	1.0643	D	120.033	r_2	0.9419
				r_{h2}	1.0628	τ	86.117	γ	101.832
H	NH ₂	-EHF	95.63099	r_n	1.7381	α_1	94.486	r_1	1.0116
		-EUMP2	95.99351	r_x	2.0286	α_2	90.074	β	104.412
				r_{h1}	1.0619	D	120.282	γ	108.612
				r_{h2}	1.0620	τ	87.539		
H	PH ₂	-EHF	381.93181	r_n	1.8984	α_1	95.369	r_1	1.4173
		-EUMP2	382.22843	r_x	2.4065	α_2	94.886	β	94.134
				r_{h1}	1.0620	D	120.220	γ	97.417
				r_{h2}	1.0627	τ	84.567		
F	OH	-EHF	214.42242	r_n	1.7949	α_1	84.949	r_1	0.9456
		-EUMP2	214.97188	r_x	1.9900	α_2	89.694	β	112.910
				r_{h1}	1.0610	D	119.779		
				r_{h2}	1.0610	τ	97.465		
F	SH	-EHF	537.11261	r_n	1.9769	α_1	91.935	r_1	1.3332
		-EUMP2	537.59407						

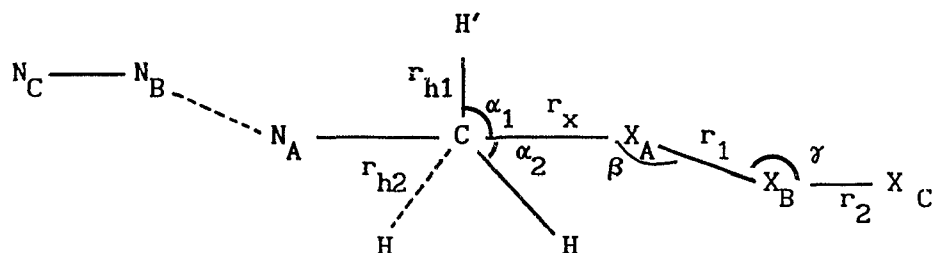
				r_x	2.3309	α_2	93.876	β	98.620
				r_{h1}	1.0622	D	119.598		
				r_{h2}	1.0607	τ	87.166		
F	NH ₂	-EHF	194.56628	r_n	1.7615	α_1	90.019	r_1	1.0120
		-EUMP2	195.10544	r_x	2.1442	α_2	84.951	β	104.241
				r_{h1}	1.0612	D	120.311	γ	112.705
				r_{h2}	1.0617	τ	92.729		
F	PH ₂	-EHF	480.86527	r_n	1.8894	α_1	91.170	r_1	1.4193
		-EUMP2	481.34072	r_x	2.5187	α_2	89.910	β	94.087
				r_{h1}	1.0611	D	120.176	γ	99.646
				r_{h2}	1.0619	τ	89.590		
Cl	OH	-EHF	574.49779	r_n	2.1025	α_1	76.691	r_1	0.9457
		-EUMP2	574.99288	r_x	2.2673	α_2	83.817	β	123.228
				r_{h1}	1.0628	D	120.286		
				r_{h2}	1.0623	τ	107.474		
Cl	SH	-EHF	897.19972	r_n	2.2823	α_1	85.767	r_1	1.3344
		-EUMP2	897.62048	r_x	2.6016	α_2	87.297	β	98.280
				r_{h1}	1.0624	D	119.770		
				r_{h2}	1.0615	τ	93.407		
NC	OH	-EHF	207.29122	r_n	2.0264	α_1	83.879	r_1	0.9457
		-EUMP2	207.93412	r_x	2.0129	α_2	89.336	β	114.760

				r_{h1} 1.0616	D 119.772	r'_1 1.1514
				r_{h2} 1.0614	τ 93.155	
NC	SH	-EHF 529.98341 -EUMP2 530.55630	r_n 2.1977	α_1 89.854	r_1 1.3335	
			r_x 2.4184	α_2 91.590	β 98.166	
			r_{h1} 1.0625	D 119.668	r'_1 1.1530	
			r_{h2} 1.0612	τ 90.978		
HO	SH	-EHF 513.08058 -EUMP2 513.57840	r_n 2.1194	α_1 94.117	r_1 1.3332	
			r_x 2.2872	α_2 95.120	β 98.341	
			r_{h1} 1.0626	D 119.363	r'_1 0.9460	
			r_{h2} 1.0609	τ 81.692	β' 115.983	
4.2.2 At the MP2 level.						
H	OH	-EUMP2 115.85549	r_n 1.8034	α_1 92.709	r_1 0.9699	
			r_x 1.8211	α_2 97.625	β 104.229	
			r_{h1} 1.0755	D 119.427		
			r_{h2} 1.0763	τ 85.349		
H	SH	-EUMP2 438.47622	r_n 1.9518	α_1 98.230	r_1 1.3336	
			r_x 2.1830	α_2 100.303	β 94.127	
			r_{h1} 1.0771	D 119.386		
			r_{h2} 1.0759	τ 81.493		
H	NH ₂	-EUMP2 95.99473	r_n 1.7123	α_1 97.386	r_1 1.0258	

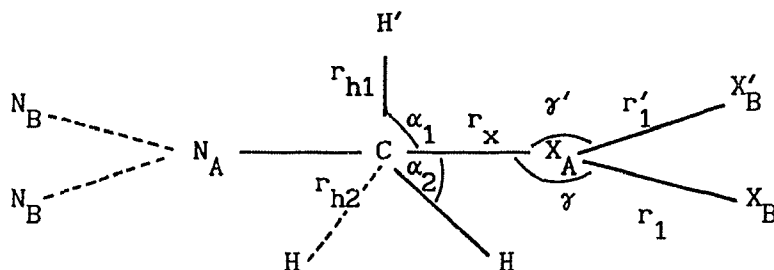
			r_x 1.9416	α_2 92.169	β 104.097
			r_{h1} 1.0761	D 120.337	γ 105.416
			r_{h2} 1.0760	τ 84.689	
H	PH ₂	-EUMP2 382.22995	r_n 1.8224	α_1 97.407	r_1 1.4153
			r_x 2.3224	α_2 96.622	β 93.609
			r_{h1} 1.0747	D 120.354	γ 95.671
			r_{h2} 1.0758	τ 82.226	
F	OH	-EUMP2 214.97300	r_n 1.7601	α_1 83.109	r_1 0.9692
			r_x 2.0084	α_2 88.650	β 108.202
			r_{h1} 1.0749	D 119.739	
			r_{h2} 1.0749	τ 94.073	
F	SH	-EUMP2 537.59468	r_n 1.8868	α_1 90.070	r_1 1.3350
			r_x 2.3283	α_2 91.742	β 95.780
			r_{h1} 1.0750	D 119.543	
			r_{h2} 1.0733	τ 89.286	
F	NH ₂	-EUMP2 195.10604	r_n 1.7101	α_1 88.366	r_1 1.0263
			r_x 2.1782	α_2 82.033	β 103.698
			r_{h1} 1.0756	D 120.401	γ 110.727
			r_{h2} 1.0760	τ 95.110	

4.3 C₂ symmetry

Geometry parameters are defined in scheme 4.3.



dihedral angle D_1 ($H'CX_A X_B$), D_2 ($CX_A X_B C$) and D ($H'CX_A H$).



dihedral angle D_1 ($H'CX_A X_B$), D_2 ($H'CX_A X'_B$) and D ($H'CX_A H$).

Scheme 4.3

4.3.1 Results at the HF and MP2' level.

HO	OH	-EHF	190.39255	r_x	1.9306	α_1	90.921	r_1	0.9455
		-EUMP2	190.95831						
				r_{h1}	1.0610	α_2	86.603	β	111.033
				r_{h2}	1.0613	D	120.296	D_1	65.754
HS	SH	-EHF	835.77905	r_x	2.4736	α_1	90.313	r_1	1.3336
		-EUMP2	836.20418						
				r_{h1}	1.0609	α_2	88.829	β	97.599
				r_{h2}	1.0618	D	120.243	D_1	56.476
HOO	OOH	-EHF	339.94196	r_x	1.8924	α_1	91.230	r_1	1.4323

				r_{h1}	1.0629	α_2	88.341	β	103.960
				r_{h2}	1.0647	D	119.800	r_2	0.9417
								γ	101.945
								D_1	62.300
								D_2	180.000
H_2N	NH_2	-EHF	150.68312	r_x	2.0339	α_1	88.276	r_1	1.0118
		-EUMP2	151.23093	r_{h1}	1.0622	α_2	87.765	γ	110.107
				r_{h2}	1.0621	D	119.798	r'_1	1.0115
								γ'	109.747
								D_1	177.760
								D_2	63.428
H_2P	PH_2	-EHF	723.28566	r_x	2.5731	α_1	90.010	r_1	1.4185
				r_{h1}	1.0624	α_2	89.781	γ	96.430
				r_{h2}	1.0620	D	119.852	r'_1	1.4184
								γ'	96.401
								D_1	168.338
								D_2	73.510

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