VIRIAL PARTITIONING: THEORY AND APPLICATIONS
THE VIRIAL PARTITIONING THEORY AND ITS APPLICATIONS
TO MOLECULAR SYSTEMS

by

ROBERT ROSS MESSER, B.Sc.

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AUTHOR: Robert Ross Messer, B.Sc. (University of Windsor) 

SUPERVISOR: Professor R. F. W. Bader 

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ABSTRACT

This thesis is concerned with the application of the theory of virial partitioning of a molecular system and its properties. In this theory the partitioning surfaces are defined in terms of the topographical features of the observable molecular charge distribution, \( \rho(r) \). Specifically, \( \rho(r) \) is partitioned by those closed surfaces through which the flux of \( \nabla \rho(r) \) is everywhere zero, i.e.,

\[
\nabla \rho(r) \cdot \hat{n}(r) = 0 \quad \forall r \in S(r) \quad (A.1)
\]

where \( \hat{n}(r) \) is the vector normal to the surface \( S(r) \) at the point \( r \). Equation (A.1) has been derived as a boundary condition through the application of the variational principle in the definition of a quantum subspace. The virial partitioning of a molecular system is obtained by constructing for the system all surfaces which satisfy equation (A.1). This set of surfaces divides a molecule into a set of chemically identifiable atomic-like fragments. Each fragment so defined possess a unique set of quantum properties; the hypervirial and virial theorems are obeyed and all properties of the fragment including its total energy are rigorously defined. Any property of the total molecular system may be equated to a sum of contributions from the spatially defined fragments. The calculated properties of the fragments, as demonstrated in this thesis, coincide with expectations based on experimental chemistry.
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This Thesis is Dedicated
to Lori
INTRODUCTION

The atomic concept of matter stretches back in time to its probable origin in early Greek philosophy. However, the atomic theory had no practical significance in chemistry until the work of John Dalton who, in the early 1800's, revived and put on firm experimental foundations the atomic nature of chemical compounds. During the ensuing period atomism played a fundamental role in the development of basic modern chemistry. Properties of a molecule were related to those of its constituent atoms. Early additivity schemes were expressed in terms of atomic contributions.

In 1916, G. N. Lewis introduced the idea of an electron pair bond, and in so doing focused attention on the interactions between atoms. Subsequent refinements to and successful applications of the concept of the "chemical bond" led to a gradual transition in thinking from "atoms" to "bonds". With the formulation and development of molecular orbital theory and quantum mechanical calculations directed at explaining the chemical bond this transition was virtually completed.

While one cannot deny the important role played by the bond concept, there exists a serious difficulty inherent in its implementation into a theoretical scheme. A chemical bond cannot be rigorously defined in the general case. A rigorous definition is implied to be one which is independent of any model and which can be stated in terms of physical quantities in real space. Consider
for example, H₂C=O, the formaldehyde molecule. What exactly constitutes the C=O or the C-H bond in this molecule? Is there any boundary separating the C=O from the H-C bond? Being unable to precisely define a bond, one must question the meaning of the many closely related concepts, including bond strengths, bond orders, bond energies, etc.

In this thesis an alternate approach to the study of chemical systems is proposed. Entitled "The Virial Partitioning Theory", the present approach is a return to the "atoms in molecules" concept. Rather than bonds, mononuclear fragments become the fundamental units of the system. The fragments described by this theory have the advantages that (1) they are uniquely defined by spatial features of the 3-dimensional charge distribution and, consequently can, in principle, be experimentally determined, and (2) they are the quantum mechanical subregions of a total system and, as a result, possess a set of rigorously defined properties. The basic premise underlying the Virial Partitioning Theory is that the distribution of charge within the fragment and, hence, the properties of the fragment are governed primarily by the nucleus in that fragment. The justification is supplied by the experimentalists who are able to detect and identify atomic-like species within molecules and who observe the often remarkable constancy of properties of functional groups in different chemical environments.

The name "Virial Partitioning" signifies the fact that each of the fragments in the partitioned system (virial frag-
ments) obeys the quantum mechanical virial theorem. This important theorem relates the kinetic and potential energies of a fragment and, further, allows the total energy of the system to be expressed as a sum of the fragment energies. Chapter 1 details the theoretical development of the partitioning theory and the conditions which must be met in order that the fragment virial theorem be obeyed. Chapters 2 to 5 are each concerned with applications of the virial partitioning theory to problems of chemical interest.
CHAPTER 1

THE VIRIAL PARTITIONING THEORY

(A) The Virial Theorem

The virial theorem is of fundamental importance in both classical and quantum mechanics as it relates the average kinetic energy, $\overline{T}$, to the average potential energy, $\overline{V}$, of a system. In its original formulation in classical mechanics, the virial theorem took the form

$$ \overline{T} = -\frac{1}{2} \sum \frac{1}{i} (\overline{r}_i \cdot \overline{v}_i) v = \frac{1}{2} \overline{V} $$

(1.1)

where the bars denote a time-averaging and the summation is over moving particles. In equation (1.1), $V$ is the classical potential energy and $\overline{V}$ represents the time-averaged total virial of the system, that is, the time average of the scalar product of the force acting on each particle with the particle's displacement from some origin. (For a closed system the time averaged force on each particle is zero, i.e., $\overline{F}_i = -\overline{V}_i v = 0$, and equation (1.1) is then invariant to any choice of origin used to define $\overline{r}_i$.) If $V$ is a homogeneous function of degree $n$, then through the application of Euler's theorem*, the average total virial and the average potential energy are related by

$$ \overline{V} = -n \overline{V} $$

________________________

*Euler's theorem states: If $\mu(x_1, x_2, \ldots, x_n)$ is a homogeneous function of degree $m$ and has continuous first partial derivatives, then

$$ \sum \frac{x_i}{x_j} \frac{\partial \mu}{\partial x_j} = m \mu $$

4
and the virial theorem takes on the simplified form of
\[ -\overline{T} = -\frac{i}{\hbar} \overline{V} = \frac{1}{2} \overline{U} \] (1.2)

Slater\(^{(5)}\) was the first to show that the virial theorem is also valid within the framework of quantum mechanics, however, a subsequent and more general derivation to that given by Slater proceeds via the hypervirial theorem\(^{(6)}\); a mathematical statement of which is given by
\[ \langle [\hat{H}, \hat{A}] \rangle = 0. \] (1.3)

In the above equation \(\hat{H}\) represents the Hamiltonian operator for a system in a stationary state and \(\hat{A}\) is any linear operator not involving time. If \(\hat{A}\) is chosen to be \(-i(\hbar/2\pi) \sum_{i} \overline{r}_{i} \cdot \overline{v}_{i}\), the evaluation of the commutator in equation (1.3) leads to the quantum mechanical analogue\(^{(7)}\) of equation (1.1). In the quantum expression of the virial theorem \(V\) is replaced by the corresponding potential energy operator, \(\hat{V}\), and the bars denote space averages rather than time averages.

Equation (1.2) is a general statement of the virial theorem. For the particular case of an isolated molecular system in which only coulombic forces are operative; the potential energy function, \(V\), is homogeneous of degree \(-1\) with respect to electron and nuclear coordinates. Hence, the molecular virial theorem may be expressed as
\[ -2 \overline{T} = \overline{V} \] (1.4)

If the Born-Oppenheimer approximation\(^{(8)}\) is valid (as is assumed in this work) then one need consider only the electronic component of the average kinetic energy, \(\overline{T}\).

The specific form of the function \(V\) includes contributions
from each of the electrostatic interactions present in the system. Consequently, the average potential energy \( \overline{V} \) may be written as

\[
\overline{V} = \overline{V'} + \overline{V''} + V_n - \sum_\alpha \overrightarrow{R}_\alpha \cdot \overrightarrow{E}_\alpha^T
\]  \hspace{1cm} (1.5)

where \( \overline{V'} \) represents the average energy of attraction between electrons and nuclei (the average one-electron potential energy), \( \overline{V''} \) represents the average energy of repulsion between electrons (the average two-electron potential energy); \( V_n \) represents the energy of repulsion between nuclei (the nuclear potential energy); \( \overrightarrow{R}_\alpha \) represents the position vector of nucleus \( \alpha \); \( \overrightarrow{E}_\alpha^T = \overrightarrow{F}_\alpha^{E}(\text{Electronic}) + \overrightarrow{F}_\alpha^N (\text{nuclear}) \) represents the total force on nucleus \( \alpha \) (the vector sum of the electronic and nuclear forces operating on \( \alpha \)). The term \(-\sum_\alpha \overrightarrow{R}_\alpha \cdot \overrightarrow{E}_\alpha^T\) represents the virial of the total force acting on each nuclear center and vanishes at equilibrium molecular geometries where the total force on each nucleus is zero.

The explicit forms of the kinetic and potential energy functions in terms of the first or second order density matrix \( \rho \) are as follows:

\[
\overline{\mathbf{T}} = \int \left[-\frac{1}{2} \mathbf{v}^2 \tau^{(1)}(\mathbf{r}, \mathbf{r}') \right] \mathbf{r}'=\mathbf{r} \, d\mathbf{r}
\]  \hspace{1cm} (1.6)

\[
\overline{V'} = \sum_\alpha \int \tau^{(1)}(\mathbf{r}; \mathbf{r}) / r_\alpha \, d\mathbf{r}
\]  \hspace{1cm} (1.7)

\[
\overline{V''} = \int \int \tau^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) / \mathbf{r}_{12} \cdot d\mathbf{r}_{1} d\mathbf{r}_{2}
\]  \hspace{1cm} (1.8)

\[
\overrightarrow{F}_\alpha = 2_\alpha \int \tau^{(1)}(\mathbf{r}; \mathbf{r}) / r_\alpha^3 \, d\mathbf{r}
\]  \hspace{1cm} (1.9)

The vector \( \overrightarrow{F}_\alpha \) is defined as \( \overrightarrow{F}_\alpha = \overrightarrow{F} - \overrightarrow{R}_\alpha \).

*The elements of the first order density matrix, \( \tau^{(1)}(\mathbf{r}, \mathbf{r}') \), and the second order density matrix, \( \tau^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \), are defined with the normalization factors \( N \) and \( N(N-1)/2 \) respectively, where \( N \) is the number of electrons.*
The equations developed to this point are applicable to isolated systems whose properties are calculated as averages taken over all space. It has been proposed in a recent series of papers by Bader and co-workers\(^{(10,11,12)}\) that a virial relationship of the form of equation (1.5) is also satisfied for certain subregions of space. The nature and shape of these subregions or fragments is determined completely by the properties of the three-dimensional electronic charge distribution \(\rho(\vec{r})\), where \(\rho(\vec{r})\) is given by the diagonal elements of the first order density matrix,

\[
\rho(\vec{r}) = r^{(1)}(\vec{r}, \vec{r})
\]

It has further been shown\(^{(13)}\) that when certain theoretical constraints are satisfied, these same fragments obey the hypervirial theorem for the operator \(\hat{\mathbf{r}} \cdot \mathbf{V}\). The conditions for the fragment virial theorem will now be developed.

(B) Conditions for a Fragment Virial Theorem

The derivation of the fragment virial theorem parallels the original proof of the molecular virial theorem given by Slater\(^{(5)}\) in 1933. The Schrödinger equation is written as

\[
\sum_{i} \left(-\frac{1}{2} \nabla^2_{i} \psi + (V - E) \psi \right) = 0
\]

(1.10)

where \(\psi\) is the electronic wavefunction and \(E\) is the total energy. On operating with \(\nabla_{j}\), taking the scalar product with \(\vec{r}_{j} \psi^{*}\) and replacing \(\psi^{*}(V - E)\) with \(\frac{1}{2} \sum_{i} \nabla^2_{i} \psi^{*}\), equation (1.10) becomes

\[
\sum_{i} \left(-\frac{1}{2} \nabla^2_{i} \psi_{j} \psi + \nabla^2_{i} \psi^{*} \psi \right) + \vec{r}_{j} \cdot \nabla_{j} \psi^{*} \psi = 0
\]

(1.11)
Using the identity*(5) *

\[
\sum_{i} \left( -\frac{1}{2} v_{i} \left[ \psi^{*2} \cdot v_{i} (\hat{r}_{j} \cdot \nabla_{j} \psi / \psi^{*}) \right] \right) + \psi^{*} v_{j}^{2} \psi \\
= \sum_{i} \left( -\frac{1}{2} \hat{r}_{j} \cdot (\psi^{*} v_{i}^{2} v_{j} \psi - v_{i}^{2} \psi^{*} v_{j} \psi) \right) \tag{1.12}
\]

equation (1.11) can be written in the more convenient form

\[
\sum_{i} \left( -\frac{1}{2} v_{i} \left[ \psi^{*2} \cdot v_{i} (\hat{r}_{j} \cdot \nabla_{j} \psi / \psi^{*}) \right] \right) + \psi^{*} v_{j}^{2} \psi + \hat{r}_{j} \cdot v_{j} \nabla \psi \psi = 0. \tag{1.13}
\]

Integration of equation (1.13) over all space gives the quantum mechanical equivalent of equation (1.1) and is just the result obtained by Slater*(5). If, instead, the coordinates of electron \( j \) are integrated over the domain of a fragment \( \Omega \) and the coordinates of the remaining electrons are integrated over all space then equation (1.13) becomes

\[
\int_{\Omega} d\mathbf{r}_{j} \int d\mathbf{r}' \left( -\frac{1}{2} v_{j} \left[ \psi^{*2} \cdot v_{j} (\mathbf{r}_{j} \cdot \nabla_{j} \psi / \psi^{*}) \right] \right) + \psi^{*} v_{j}^{2} \psi + \mathbf{r}_{j} \cdot v_{j} \nabla \psi \psi = 0 \tag{1.14}
\]

where \( \int d\mathbf{r}' \) denotes integration over all space of all electrons except the \( j \)th electron. Because the wavefunction and its derivatives vanish at infinity, every term in the sum over \( i \), except for \( i = j \), vanishes in the integration. Using a form of Green's theorem (Green's first identity) the volume integral over the fragment \( \Omega \) can be expressed as an integral over the

*Note that the form of (1.12) is altered slightly from that used by Slater*(5).
surface \( S(\Omega) \) bounding \( \Omega \).

\[
- \frac{1}{2} \int_{\Omega} \int_{S(\Omega)} \left[ \phi^* \phi \cdot \nabla_j \left( \hat{r}_j \cdot \nabla_j \psi / \psi^* \right) \right] \cdot dS_j \\
+ \int_{\Omega} \int \left[ \phi^* \phi \cdot \nabla_j \left( \psi \nabla_j \psi^* \right) + \hat{r}_j \cdot \nabla_j \hat{V} \psi \psi^* \right] = 0 \quad \text{(1.15)}
\]

On carrying out the first differentiation indicated by \( \nabla_j \) and summing the equation over \( j \) so that all electrons are treated in an equivalent manner, equation (1.15) becomes

\[
- \frac{1}{2} \int_{\Omega} \int_{S(\Omega)} \left[ \phi^* \phi \cdot \nabla_j \left( \hat{r}_j \cdot \nabla_j \psi \right) - \psi \psi^* \left( \hat{r}_j \cdot \nabla_j \psi \right) \right] \cdot dS_j \\
+ \sum_{j} \int_{\Omega} \int \left[ \phi^* \phi \cdot \nabla_j \left( \psi \nabla_j \psi^* \right) + \hat{r}_j \cdot \nabla_j \hat{V} \psi \psi^* \right] = 0 \quad \text{(1.16)}
\]

Being careful of normalization constants (see footnote at the bottom of page 6), equation (1.16) can be expressed in terms of the first and second order density matrices as

\[
- \frac{1}{2} \int_{S(\Omega)} dS \cdot \left[ \nabla_1 (\hat{r}_1 \cdot \nabla_1) - \nabla_1 \cdot (\hat{r}_1 \cdot \nabla_1) \right] r^{(1)}(r; r') r' \text{d}r' \\
+ \int_{\Omega} dV_1 \cdot \nabla_1 r^{(1)}(r; r') r' \text{d}r' \\
- \frac{1}{a} \sum_{\alpha} \int_{\Omega} \hat{r}_1 \cdot \nabla_1 r^{(1)}(r; r) r \text{d}r \\
+ \frac{1}{a} \int_{\Omega} \int dV_2 \hat{r}_2 \cdot \nabla_2 r^{(2)}(r_1, r_2) r_1 r_2 = 0 \quad \text{(1.17)}
\]

where the potential energy operator \( \hat{V} \) has been separated into its one and two electron components.

Consider, now, each of the terms in equation (1.17). The
first term - let it be denoted by \( S_1(\Omega) \) is an origin dependent quantity due to the presence of \( r_1 \). Also, its evaluation assumes a knowledge of the specific form of the partitioning surface bounding the fragment \( (\Omega) \).

Apart from a factor of 2, the second term in equation (1.17) has a form analogous to that of the kinetic energy expression of equation (1.6). This term then, corresponds to twice the average kinetic energy of the fragment - \( 2\bar{T}(\Omega) \).

The third term can be simplified to some extent by the following application of Euler's theorem

\[
\sum_{\alpha} \mathbf{r}_{1\alpha} \cdot \nabla_{\mathbf{r}_{1\alpha}}^{-1} + \sum_{\alpha} \mathbf{R}_{\alpha} \cdot \nabla_{\mathbf{r}_{1\alpha}}^{-1} - \mathbf{r}_{1\alpha}^{-1} = \mathbf{r}_{1\alpha}^{-1} \quad (1.18)
\]

Substitution of the above equation into the third term of equation (1.17) leads to

\[
-\sum_{\alpha} \int_{\Omega_{\alpha}} \mathbf{d}r_{1\alpha} \mathbf{r}_{1\alpha} \cdot \nabla_{\mathbf{r}_{1\alpha}}^{-1} T^{(1)}(\mathbf{r}; \mathbf{r}) = \sum_{\alpha} \int_{\Omega_{\alpha}} \mathbf{d}r_{1\alpha} T^{(1)}(\mathbf{r}; \mathbf{r}) \mathbf{r}_{1\alpha}^{-1} \]

\[
-\sum_{\alpha} \int_{\Omega_{\alpha}} \mathbf{d}r_{1\alpha} \mathbf{R}_{\alpha} \cdot \nabla_{\mathbf{r}_{1\alpha}}^{-1} T^{(1)}(\mathbf{r}; \mathbf{r}) \quad (1.19)
\]

The first term on the RHS of equation (1.19) is analogous to equation (1.7) and, thus, corresponds to the fragment one-electron potential energy, \( V'(\Omega) \). This quantity represents the energy of interaction of each nucleus in the system with the charge density in the fragment \( (\Omega) \). (It is often useful to express \( V'(\Omega) \) as a sum of contributions from each nuclear center. If the specific interaction of nucleus \( \alpha \) with the charge density in the fragment \( (\Omega) \) is denoted by \( V'_{\alpha}(\Omega) \), then

\[
V'(\Omega) = \sum_{\alpha} V'_{\alpha}(\Omega) \quad (1.20)
\]
where the summation is over all nuclei in the system.) The second term of equation (1.19) is of the form \( \sum \vec{R}_\alpha \cdot \vec{F}_\alpha (\Omega) \) where \( \vec{F}_\alpha (\Omega) \) is the force exerted on the nucleus \( \alpha \) by the charge density in the fragment \( (\Omega) \). In terms of the charge density

\[
\vec{F}_\alpha (\Omega) = Z_\alpha \int_\Omega \left. \frac{\partial \rho (r)}{\partial r} \right|_{r_1} \frac{\vec{r}_1}{r_1^3}.
\]  

(1.21)

The quantity \( \sum \vec{R}_\alpha \cdot \vec{F}_\alpha (\Omega) \) represents the fragment contribution to the nuclear virial and will be denoted as \( -\nabla_n (\Omega) \). Because of the vector \( \vec{R}_\alpha \), the fragment nuclear virial is an origin dependent quantity.

The fourth and last term of equation (1.17) can be simplified with use of the following relation:

\[
\vec{r}_1 \cdot \nabla_1 r_{12}^{-1} + \vec{r}_2 \cdot \nabla_2 r_{12}^{-1} = -r_{12}^{-1}.
\]  

(1.22)

Upon substitution of equation (1.22) into the last term of equation (1.17) one obtains

\[
2 \int_\Omega \left[ \int_\Omega \left. \frac{\partial \rho (r)}{\partial r} \right|_{r_1} \right] (\vec{r}_1 \cdot \vec{r}_2) = -\int_\Omega \int_\Omega \frac{1}{r_{12}^3} (\vec{r}_1 \cdot \vec{r}_2)
\]

\[
+ \int_\Omega \int_\Omega \left[ \vec{r}_1 \cdot \nabla_1 - \vec{r}_2 \cdot \nabla_2 \right] r_{12}^{-1} (\vec{r}_1 \cdot \vec{r}_2).
\]  

(1.23)

The first term on the RHS of equation (1.23) represents the average two-electron potential energy of the fragment, \( \nabla'' (\Omega) \), (cf. equation (1.8)) and corresponds to the electronic repulsions within the fragment \( (\Omega) \) plus one-half of the repulsions of the electrons in \( (\Omega) \) with those in the remainder of the
system*, \((\Omega', \Omega')\). The second term in equation (1.23), \(\nabla''(\Omega, \Omega')\), is origin dependent quantity and has no analogue in the total space virial theorem.

It is now possible to rewrite equation (1.17) in the compact form of

\[
-2T(\Omega) - \left[ V'(\Omega) + V'(\Omega) + V_n(\Omega) \right] + S_1(\Omega) + V''(\Omega, \Omega') = 0 .
\]  
(1.24)

This equation is satisfied for any fragment. The terms within the square brackets constitute the total fragment virial, \(\overline{V}(\Omega)\). Thus, if the all-space form of the virial theorem is to be obeyed for a fragment, the last two quantities in equation (1.24) must vanish. As these two terms are origin-dependent, one may choose an origin which causes the sum of \(S_1(\Omega)\) and \(V''(\Omega, \Omega')\) to vanish, thereby yielding a value of \(V_n(\Omega)\) such that the virial theorem for a single fragment,

\[
-2T(\Omega) = V'(\Omega) + V''(\Omega) + V_n(\Omega) = \overline{V}(\Omega)
\]  
(1.25)

is satisfied. A much stronger condition, however, is to demand that both \(S_1(\Omega)\) and \(V''(\Omega, \Omega')\) vanish separately. As demonstrated below, this condition is met when the fragment is constrained to obey the hypervirial theorem for the operator \(\hat{T}_i \cdot \hat{V}_i\) as well as the virial theorem.

Epstein in a recent paper(14) has shown that for any

*The integration of \(\Gamma^{(2)}(r_1, r_2)/r_{12}\) over \((\Omega)\) may be written as

\[
\left( \int_{\Omega} d\Omega_1 \int_{\Omega_1} d\Omega_2 + \int_{\Omega} d\Omega_1 \int_{\Omega_1} d\Omega_2 \right) \Gamma^{(2)}(r_1, r_2) = V''(\Omega) + V'_\Omega(\Omega') = V''(\Omega)
\]

where \(\Omega'\) indicates the volume of space, excluded by \(\Omega\). \(V''(\Omega)\) is the self-repulsions of the electrons in \((\Omega)\). \(V''_{\Omega}(\Omega')\) is one-half of the electronic repulsions between \((\Omega)\) and \((\Omega')\).
operator $\hat{W}$, the following is true:

$$
\sum_i \int d\mathbf{r}_i \int d\mathbf{r'} \psi^* \left[ \hat{W} \hat{H} \right] \psi = \sum_i \left[ \int d\mathbf{r}_i \int d\mathbf{r'} \hat{H} \psi^* \hat{W} \psi - \int d\mathbf{r}_i \int d\mathbf{r'} \psi^* \hat{W} \psi \right].
$$

If the integrations are carried out over all space, the RHS of the above equation will equal zero because of the Hermitian nature of the Hamiltonian operator, $\hat{H}$. In this case, equation (1.26) becomes a statement of the hypervirial theorem. It then follows that a regional hypervirial theorem will be obeyed if

$$
\sum_i \left[ \int d\mathbf{r}_i \int d\mathbf{r'} \hat{H} \psi^* \hat{W} \psi - \int d\mathbf{r}_i \int d\mathbf{r'} \psi^* \hat{W} \psi \right] = 0.
$$

Terms involving the potential energy components of $\hat{H}$ cancel out of this equation and, with the subsequent use of Green's theorem, the equation can be reformulated as

$$
\frac{1}{2} \sum_i \int \int \int d\mathbf{S} \cdot \left[ (\nabla_j \psi^*) \hat{W} \psi - \psi^* \nabla_j (\hat{W} \psi) \right] = 0.
$$

Except for differences in notation, this is Epstein's general result (14). If $\hat{W}$ is taken to be the virial operator, $\hat{V} \cdot \nabla$, the LHS of equation (1.28) becomes equivalent to $S_1(\Omega)$. Note that Epstein's surface condition for obtaining a fragment hypervirial theorem is not sufficient to yield the corresponding fragment virial theorem. The simultaneous satisfaction of the fragment virial theorem requires that the second of the dual conditions be met, i.e., that $V''(\Omega, \Omega')$ also be equal to zero.

It has been shown numerically in a previous investigation (11) that for an arbitrary fragment of a molecular system an origin
can be found such that the surface integral $S_1(n)$ vanishes. However, the origin so defined does not yield a value of $V_n(n)$ such that the fragment virial theorem is obeyed, that is, $V''(n,n') \neq 0$. This earlier work demonstrated the necessity of another condition in addition to the choice of an origin. This second condition is the particular choice of a surface bounding the fragment. Numerical evidence has been presented\(^{(10,11)}\), which indicates that a virial relationship is satisfied for a fragment when it is bounded by a *closed* surface through which the flux of $\mathfrak{v}_n(r)$ is everywhere zero. If $S(r)$ denotes such a surface, then

$$\mathfrak{v}_n(r) \cdot \hat{n}(r) = 0 \quad \forall \ r \in S(r)$$

(1.29)

where $\hat{n}(r)$ is a unit vector normal to $S(r)$ at the point $r$.

Thus fragments bounded by a zero flux surface defined by equation (1.29) ("virial fragments") possess theoretical properties in common with the total, isolated system. These properties are: (1) the virial theorem is obeyed, and (2) the hypervirial theorem for the operator $\vec{r} \cdot \mathfrak{v}$ is obeyed within the domain of the fragment. The kinetic energy of a fragment and the virial of all the forces exerted on the fragment are related through the fragment virial theorem, equation (1.25).

When there are no external forces acting on the system, one obtains the further virial relationship*

*For the total molecular system, the nuclear virial, $\mathfrak{V}_n$, and the total energy, $E$, may be expressed as
\[-\mathbf{T}(\Omega) = \mathbf{E}(\Omega)\]  

(1.30)

where $\mathbf{E}(\Omega)$, the total energy of the fragment, is given by

\[\mathbf{E}(\Omega) = \mathbf{T}(\Omega) + \mathbf{V}'(\Omega) + \mathbf{V}''(\Omega) + \mathbf{V}_n(\Omega) = \mathbf{T}(\Omega) + \mathbf{V}(\Omega).\]  

(1.31)

Hence, for the equilibrium state, one may partition the total energy into contributions from separate spatial regions of the system, the spatial regions being the virial fragments.

It has recently been shown\(^{(15)}\) that the zero-flux surface condition, equation (1.29), is obtained as a boundary condition in the application of the quantum mechanical variational principle to the definition of a subspace of a total molecular system. Thus the "virial fragments" emerge as the quantum subspaces of a total system.

Consider, initially, the variation of the energy functional $G(\phi)$,

\[G(\phi) = \int d\mathbf{r} \left[ \frac{1}{2} \sum_j \nabla_j \phi^* \cdot \nabla_j \phi + (\mathbf{V} + \lambda) \phi^* \phi \right]\]  

(1.32)

where $\int d\mathbf{r}$ denotes $\int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N$ and the boundary conditions are defined by a surface at infinity (This corresponds to Schrödinger's original derivation of the wave equation). In equation (1.32) $\lambda$ is the Lagrangian multiplier which ensures that the constant $\int d\mathbf{r} \phi^* \phi$ = constant is obeyed.

A variation is caused in $G(\phi)$ by varying the wavefunction according to

\[\phi(\mathbf{r}) = \psi(\mathbf{r}) + \varepsilon \eta(\mathbf{r})\]  

(1.33)

\[\mathbf{V}_n = -\sum_{\alpha} \frac{\alpha \cdot \mathbf{F}_\alpha}{\mathbf{r}_\alpha} \cdot \mathbf{r} + \mathbf{V}_n \quad \text{and} \quad \mathbf{E} = -\mathbf{T} + \sum_{\alpha} \frac{\alpha \cdot \mathbf{F}_\alpha}{\mathbf{r}_\alpha}, \]

where $\mathbf{V}_n$ is the nuclear potential energy, $\sum_{\alpha} \frac{\alpha \cdot \mathbf{F}_\alpha}{\mathbf{r}_\alpha}$, and $\mathbf{F}_\alpha$ is the total force acting on the nucleus $\alpha$. For the system at equilibrium $\mathbf{F}_\alpha = 0$ for all $\alpha$ so that $\mathbf{V}_n = \mathbf{V}_n$ and $\mathbf{E} = -\mathbf{T}$. In terms of fragment quantities this means that $\mathbf{n}_n(\Omega) = \mathbf{V}_n$ and that $\mathbf{E}(\Omega)$ is given by equation (1.30).
where \( \phi(\mathbf{r}) \) is the trial function; \( \Psi(\mathbf{r}) \) is assumed to be the function which causes the variation in \( G(\phi) \) to vanish (i.e., \( \delta G(\phi) = 0 \)); \( \eta(\mathbf{r}) \) is an arbitrary differentiable function and \( \epsilon \) is a scale factor. Through the application of calculus of variations\(^{(18)}\), one obtains

\[
\delta G(\phi) = \int d\mathbf{r} \eta [\hat{H}\phi^* + \lambda \phi^*] + \sum_{j} \oint ds(\mathbf{r}_j) \int dr' \eta \left( \overrightarrow{A}(j)f \cdot \overrightarrow{n}_j \right) + \text{complex conjugate}
\]

(1.34)

where \( f \) represents the integrand of equation (1.32); \( \hat{H} \) is the Hamiltonian operator and

\[
\overrightarrow{A}(j)f = \frac{\epsilon}{k} \frac{\delta f}{\delta \Psi_j} + \frac{T}{2} \frac{\delta f}{\delta \Psi_j} + \frac{m}{\epsilon} \frac{\delta f}{\delta \Psi_j}
\]

with \( \Psi_j = \frac{\delta \Psi}{\delta X_j} \) etc. Thus the vanishing of \( \delta G(\phi) \) for an arbitrary variation in \( \Psi(\mathbf{r}) \) leads to two conditions which are both necessary and sufficient\(^{(15, 18)}\) ensure the applicability of the variational principle to all space, namely,

\[
\hat{H} \Psi + \lambda \Psi = 0
\]

(1.35)

and

\[
\overrightarrow{A}(j) \cdot \overrightarrow{n}_j = \nabla_j \Psi \cdot \overrightarrow{n}_j = 0 \quad \Psi \cdot \mathbf{r}_j \in S(\mathbf{r})
\]

(1.36)

The boundary condition of equation (1.36) is obeyed for each value of \( j \) by demanding that \( \Psi \) vanish at infinity. This equation may be regarded as a natural boundary condition which must be satisfied if \( \Psi \) is to satisfy the Euler-Lagrange equation

\[
\hat{H} \Psi = E \Psi
\]

(1.37)

where \( E( = -\lambda) \) is identified as the total energy of the system.\(^{(17)}\)

Equation (1.37) is Schrödinger's famous wave equation which is found to properly predict and describe the behaviour of matter at the microscopic level. The above development demonstrates that for a stationary state, the wavefunction \( \Psi \) which satisfies
Schrödinger's equation (and the natural boundary condition) is equivalent to finding the function $\psi$ which minimizes the total energy of the system.

The question to be asked is: are there any other boundary conditions of physical significance which when applied in the variation of the energy functional $G$ yield $\hat{H}\psi = E\psi$ as the Euler-Lagrange equation? Alternately, given $\hat{H}\psi = E\psi$, what are the surfaces which cause the energy functional $G$ to be stationary?

Consider the variation of the totally general energy functional $G(\phi, \{\Omega_i\})$:

$$G(\phi, \{\Omega_i\}) = \int_{\Omega_1} \int_{\Omega_2} \cdots \int_{\Omega_n} \left( \sum_{i=1}^n \frac{1}{2} \nabla_i \phi^* \cdot \nabla_i \phi + (\nabla - \lambda) \phi^* \phi \right)$$  \hspace{1cm} (1.38)

where $\{\Omega_i\}$ denotes a set of subspaces $- \Omega_i$ being a subspace for electron $i$ bounded by a surface $S_i(\phi)$. In this totally general variation, the boundary surface for each electron, rather than being arbitrarily fixed at infinity, is instead considered to be a function of $\phi$. Thus the surfaces are to be variationally determined in the variation of $G(\phi, \{\Omega_i\})$.

Application of the calculus of variations then yields

$$\delta G(\phi, \{\Omega_i\}) = \frac{1}{2} \left\{ \left\langle \left[ \hat{H}, \hat{\omega} \right] \right\rangle \_{\{\Omega_i\}} + \text{c.c.} \right\}$$  \hspace{1cm} (1.39)

with $\hat{H}\psi = E\psi$ as the Euler-Lagrange equation if the following natural boundary conditions are satisfied:

$$\nabla_i \phi_i(\xi_i) \cdot \hat{n}_i = 0 \quad \forall \xi_i \in S_i$$  \hspace{1cm} (1.40)

The quantities in equations (1.39) and (1.40) have the following definitions: $\hat{\omega}$ is a linear operator which causes the infinitesimal variation in $\psi$; that is, $\delta \psi = \hat{\omega} \psi$; the subscript $\{\Omega_i\}$ implies that the averaging of the commutator is carried out in the manner indicated in the definition of $G(\phi, \{\Omega_i\})$, equation
\[ R_i (x_i) = \prod_j \int \psi^* \psi \]  

with \( j \neq i \)  

Equation (1.40) is both a boundary condition which must be satisfied by \( \psi \) and an operational definition of the subspaces.

When all the \( S_i \) occur at infinity one obtains Schrödinger's original result. In this case the commutator \( \langle [\hat{H}, \hat{\omega}] \rangle \) vanishes as a consequence of the hypervirial theorem, yielding \( \delta G(\phi) = 0 \). The only other physically accessible set of boundary conditions is obtained when all \( S_i \) but one are placed at infinity (where equation (1.40) is satisfied) and the remaining surface, say \( S_1 \), is correspondingly defined by

\[ \nabla \cdot \rho_1 (x_i) \cdot n = 0 \quad \forall x_i \in S_1 \]  

(1.42)

In this case, and only in this case, \( \rho (x_i) \) reduces to the measurable electronic charge density \( \rho (x_i) \) (see equation (1.41)) and the boundary condition is identical to the zero-flux definition of the surface of a virial fragment. While the general set of boundary conditions given in equation (1.40) is of mathematical interest, only the two particular cases outlined above correspond to physically accessible situations. Hence, Schrödinger's equation may be variationally determined subject to the all space boundary conditions and to the boundary condition which defines the surface of a virial fragment.

In summary, it has been shown that the satisfaction of the variational result

\[ \delta G(\phi, \chi) = \frac{1}{2} \left\{ \langle [\hat{H}, \hat{\omega}] \rangle_{\phi} + \text{c.c.} \right\} \]  

(1.43)

for all arbitrary variations \( \delta \psi = \hat{\omega} \psi \) yields \( \hat{H} \psi = E \psi \) as the Euler-Lagrange equation (or, alternately, is equivalent to
solving Schrödinger's equation, subject to the following natural
boundary conditions:
\[ \nabla_i \Psi \cdot \mathbf{n}_i = 0 \quad \forall \mathbf{r}_i = \infty \quad i \in \{2, 3, \ldots, N\} \]
and \[ \nabla_i \rho(\mathbf{r}_i) \cdot \mathbf{n}_i = 0 \quad \forall \mathbf{r}_i \in S(r_i) \]
Equation (1.43) is a generalization of the all space variational
principle. By demonstrating that the variation of the energy
functional used by Schrödinger is equal to the value of a
corresponding commutator averaged over all space or an
appropriately defined subspace, one concludes that the all space
result is but a special case of a more general result.

Equation (1.43) may also be viewed as a generalization
of the hypervirial theorem, one which relates it directly to
the variational principle. Thus when \( \hat{\omega} \) is set equal to \(- \epsilon \mathbf{r}_i \cdot \nabla_i \),
one obtains
\[ \delta G(\Psi, \Omega) = 2 \tilde{T}(\Omega) + \tilde{V}(\Omega) = \mathcal{B} \langle \mathbf{r} \cdot \nabla \Psi, \nabla \rho \cdot \mathbf{n} \rangle = 0 \]
where
\[ \mathcal{B} \langle \mathbf{r} \cdot \nabla \Psi, \nabla \rho \cdot \mathbf{n} \rangle = 0 = \frac{1}{2} \Omega \int dS \int d\mathbf{r} \left[ \Psi^* \nabla (\mathbf{r} \cdot \nabla \Psi - \mathbf{r} \cdot \nabla \Psi \Psi^*) \right] \cdot \mathbf{n}_i \]
Through the proper choice of origin, the surface integral
may be made to vanish, yielding the subspace virial theorem,
equation (1.25). Thus the subspace virial theorem is obtained
from the vanishing of the average of the appropriate commutator
as in the all space derivation. The same choice of origin,
however, also causes of \( \delta G(\Psi, \Omega) \) to vanish, and, the variational
principle is simultaneously satisfied. This simultaneous
satisfaction of the variational principle and the hypervirial
theorem is possible only when the space "\( \Omega \)" refers to all space
or to a subspace bounded by a surface of zero-flux (equation (1.42)).
(C) The Partitioning Surfaces

One of the conditions for the existence of a quantum mechanical subspace is the requirement that the subspace be bounded by a closed surface of zero-flux. Because of the fundamental importance to Virial Partitioning Theory of this surface condition, a detailed discussion of the definition and properties of the zero-flux-surface is presented here.

In general, there are an infinite number of zero-flux surfaces permeating a molecular charge distribution; in fact, there is one such surface through any arbitrary point in the charge distribution. Only a finite number of these surfaces, however, meet the additional requirement of equation (1.29), i.e., that they be everywhere defined. All zero-flux surfaces except those bounding virial fragments terminate at a nuclear position; the site of a cusp in $\rho(r)$ and a point at which $\nabla \rho(r)$ is not defined. Thus a virial fragment can never be bounded by a surface containing nuclei.

The zero-flux surface can be computed in terms of a set of gradient paths. These are paths traced out by the vector $\nabla \rho(r)$ and correspond to the lines of "steepest ascent" through a charge distribution. It is clear, then, that from any arbitrary point in $\rho(r)$, the line of $\nabla \rho(r)$ will be directed toward and will terminate at cusps coincident with nuclear positions in the charge distribution. In certain special cases $\nabla \rho(r)$ will be directed, not toward a nuclear cusp, but toward a "null or stationary point" (a point at which $\nabla \rho(r) = 0$)
within the distribution of charge.

To digress for a moment — a null point is usually found within a charge distribution between a pair of "bonded" nuclei ("bonded" is used in the traditional chemical sense) and is located at the minimum point along the "ridge" of maximum charge density between the nuclei.* Apart from their internuclear positions, null points are also found at relative minima in \( \rho(r) \) — for example, there is a null point located at the center of the benzene molecule. Further, any isolated charge distribution is completely bounded by null points at infinity by virtue of the fact that at \( r = \infty \), \( \rho(r) = \nabla \rho(r) = 0 \).

The zero-flux partitioning surface of equation (1.29) can be alternately but equivalently defined as: the set of gradient paths which both originate and terminate at null points in the charge distribution. In most simple molecular systems the gradient paths bounding virial fragments generally originate at infinity and terminate at internuclear null points.

The degree of subdivision to which a charge distribution can be partitioned into quantum subspaces is limited by the number of null points in the distribution (excluding those at infinity). For an isolated atom, \( \rho(r) \) is centro-symmetric; there are no null points and, therefore, an atom cannot be partitioned into smaller quantum fragments. A diatomic mole-

*This internuclear null point is often referred to as a "saddle point" in the charge distribution. Saddle points are a particular subset of the more general set of null points.
cule with its one internuclear null point can be subdivided to yield two, and no more than two, quantum fragments. In general, any N-centered molecular system \((N \neq 1)\) can be maximally partitioned into \(N\) quantum subspaces; each containing a single nuclear center. Thus the result of the virial partitioning procedure is to divide a molecule into a collection of single-center or atomic-like fragments.

Since the partitioning surfaces are determined solely by the topography of the charge density, the shapes of these surfaces can provide information concerning the distribution of charge in a molecule. Illustrated in Figure 1.1 are the partitioning surfaces in four families of neutral, ground state, diatomic molecules. The position of the reference nucleus of each family is held fixed and the surfaces are plotted relative to this point. Because of the axial symmetry in these molecules only the upper half of each surface is shown. If, in the molecule \(AB\), there is a transfer of most all the valence charge density from \((A)\) to \((B)\), the molecule is characterized by a partitioning surface which is paraboloid in shape and which curves so as to encompass the \(A\) fragment - the fragment of net positive charge. Such a situation usually occurs when the number of valence electrons in \(A\) is equal to or less than the number of vacancies in the valence shell of \(B\). Thus, for example, in the hydride and fluoride families the surfaces of \(LiH\) and \(LiF\) are shaped in the manner described; as are the surfaces in \(LiO\) and \(BeO\) in the oxide series. The decreased
electronegativity of N and, as a consequence, the incomplete transfer of valence density to (N) from both (B) in BN and, to a lesser extent, (Be) in BeN, is reflected by the non-parabolic shape of \( S(r) \) in these molecules. For a second class of molecules, those in which the number of valence electrons on A exceeds the number of vacancies on B, charge transfer from (A) to (B) is reflected in the initial paraboloid nature of \( S(r) \) starting from the internuclear null point; however, the diffuse valence density in (A) causes a reversal in the curvature of the outer arms of the surface \( S(r) \). This is the case for the following molecules: BeH, BeF, BH, BF, BO, CQ and CF.

In the limit of A being identical to B, the form of \( S(r) \) is a plane perpendicular to the bond axis. In the AF, AO and AN families of molecules the approach to this limit by NF and NO is apparent from the nearly planar surfaces in these two molecules.

The set of surfaces in the AH series illustrates particularly well the relationship between the shape of \( S(r) \) and the charge transfer within the system. The increasing electronegativity of A from Li to F is reflected in the charge distributions of the hydrides as a sweep in the curvature of \( S(r) \) throughout the series in accordance with the corresponding decreasing amount of charge contained within (H).

* The partitioning surfaces as well as the virial fragment properties were numerically calculated using a set of computer programs developed in this laboratory. They are reported in the thesis of G.R. Runtz. (64)
Figure 1.1

The partitioning surfaces for families of neutral, ground state, diatomic molecules. The surfaces are plotted with respect to a fixed position of the reference nucleus in each family. Because of axial symmetry only the upper half of each surface is shown.

Upper left - surfaces for diatomic fluorides.
Upper right - surfaces for diatomic oxides.
Lower left - surfaces for diatomic hydrides.
Lower right - surfaces for diatomic nitrides.
CHAPTER 2

THE CHEMICAL SIGNIFICANCE OF VIRIAL FRAGMENTS

(A) Chemical Properties of Virial Fragments

A prime objective of molecular partitioning is to attain some explanation of the often observed retention of group or atomic properties within molecules. For example, the cyano group has a characteristic set of properties (e.g. dipole moment, electron affinity, force constant) which vary only slightly in a great number of molecules. This retention of properties is, in many cases, so close as to give rise to additivity schemes in certain molecular systems. (19)

One of the early observations which ultimately led to the virial partitioning theory was the similarity of the charge distributions in those fragments whose properties were nearly transferable. (20) The implication here is that the charge density is the carrier of information. A theorem by Hohenberg and Kohn (21) supplies the theoretical basis for this notion, as these authors have demonstrated that the total energy of a system is, in principle, a unique functional of the charge density; at least in the case of non-degenerate ground states. Since the virial partitioning theory defines a fragment in terms of the topological features of the charge distribution it naturally accounts for the constancy of fragment properties in those cases where only small changes in the charge density are observed. A virial fragment maximizes the possible trans-
fer of properties because the zero-flux surface - by the nature of its definition in terms of \( \rho(r) \) - maximizes the extent to which the distribution of charge of the fragment is transferable between systems. Any other choice of surface will either include part of the neighbouring fragment which may change radically on transfer, or will omit a portion of its own charge density, which changes little on transfer. *

The concept of property transferability can be put on a more quantitative level via the fragment virial theorem. For the kinetic energy of a fragment, and if the system is in equilibrium, for the total energy of a fragment to be identical in two systems requires that the sum of the virial of all forces exerted on the fragment be identical in the two systems. The total fragment virial, \( \nu(\Omega) \), may be broken up into an inner virial, \( \nu^i(\Omega) \), the virial of all forces originating from within the fragment, and an outer virial, \( \nu^o(\Omega) \), the contribution from all forces external to the fragment. For an equilibrium situation

---

*An alternate proposal of molecular partitioning is the "loge theory" of Daudel and co-workers \((22,23)\) based on information theory. A loge represents a region of physical space such that the "best" division of a system into loges is that which maximizes the possible knowledge of the system. \((24,25)\) In a recent comparison of the two theories \((26)\) it was found that in cases where the localization of charge density is well defined by "deep minima" the best loges correspond to the virial fragments. In those cases where the minima in \( \rho(r) \) are less pronounced, the best loges appear as close approximations to the virial fragments. See Appendix A1 for further details of the loge theory.
\[ E(\Omega) = - \bar{T}(\Omega) = \frac{1}{2} \left[ \bar{v}^i(\Omega) + \bar{v}^o(\Omega) \right] \]  

(2.1)

The inner virial is determined solely by the quantum properties within the fragment. Thus if a fragment is to possess identical properties in two systems, the outer virial of the fragment must be identical in both systems. It is important to realize that only the sum of the outer virials need be identical; the individual contributions may vary considerably.

The determination of \( T(\Omega) \) requires a knowledge of \( r^{(1)}(\mathbf{r}; \mathbf{r}') \) everywhere within the fragment and of the values of its derivatives at each point in the surface. Since \( T(\Omega) \) is related to the inner and outer virials, the former being determined entirely by the fields within \( (\Omega) \), one concludes that the information contained in the external virial is equivalent to a knowledge of the derivatives of \( r^{(1)}(\mathbf{r}; \mathbf{r}') \) in the surface.

To further illustrate the ideas presented above, specific numerical examples of a variety of chemical systems are analyzed in some detail in the following sections.

(i) **Hydride Systems.**

The hydrogen fragment is unique among chemical fragments in that it possesses no core electrons. As a consequence of this the entire \( H \) fragment charge density is highly sensitive to changes in external fields. This is particularly evident from the plots in Figures 2.1 and 2.2 showing the ground state charge distributions and virial fragments of the 1st and 2nd row diatomic hydrides respectively. Note the
Figure 2.1

Contour maps\textsuperscript{a} of the electronic charge densities for the first row neutral diatomic hydrides. The virial partitioning surfaces are indicated by dashed lines. The maps correspond as follows:

\begin{align*}
\text{LiH (} X^1\Sigma^+ \text{)} & \quad \text{CH (} X^2\Pi_r \text{)} \\
\text{BeH (} X^2\Sigma^+ \text{)} & \quad \text{NH (} X^3\Sigma^- \text{)} \\
\text{BH (} X^1\Sigma^+ \text{)} & \quad \text{OH (} X^2\Pi_1 \text{)} \\
\text{FH (} X^1\Sigma^+ \text{)} & \end{align*}

\textsuperscript{a}The contours in this figure and in all other maps of the electronic charge density increase in value (in au) from the outermost contour inwards in steps of 2 x 10\textsuperscript{n}, 4 x 10\textsuperscript{n}, and 8 x 10\textsuperscript{n}. The smallest contour value is 0.002 with \( n \) increasing in steps of unity to yield a maximum contour value of 20.
Figure 2.2

Contour maps of the electronic charge densities for the second row neutral diatomic hydrides. The virial partitioning surfaces are indicated by dashed lines. The maps correspond as follows:

\[
\begin{align*}
\text{NaH} & \quad (X^1\Sigma^+) \\
\text{MgH} & \quad (X^2\Sigma^+) \\
\text{SiH} & \quad (X^2\Pi) \\
\text{SiH} & \quad (X^2\Pi) \\
\text{AlH} & \quad (X^1\Sigma^+) \\
\text{PH} & \quad (X^3\Sigma^-) \\
\text{ClH} & \quad (X^1\Sigma^+)
\end{align*}
\]
radical difference in shape of the $H$ fragments of the alkali hydrides, LiH and NaH, on the one hand, and the halogen hydrides, FH and ClH, on the other. This malleable nature of the charge distribution in $(H)^+$ gives rise to large variations in the fragment properties. An excellent representative example is the population, $\bar{N}(H)$, defined as

$$\bar{N}(\Omega) = \int_{\Omega} \rho(r) \, dr$$

(2.2)

where, in this case, $\Omega$ refers to the $H$ fragment. It is often convenient to consider instead of the population, the net charge associated with the fragment, $\overline{C}(\Omega)$. The two quantities are related by

$$\overline{C}(\Omega) = Z_{\Omega} - \bar{N}(\Omega)$$

(2.3)

where $Z$ is a nuclear charge. The net charges of $(H)$ are recorded in Table 2.1 which contains partitioning results for the hydride series of molecules. It is seen from this table that $\overline{C}(H)$ varies from a value of -0.911 in LiH, indicating a charge transfer of nearly one electron from the lithium to the hydrogen fragment, to a value of +0.760 in HF. (In the species HeH$^+$ and FH$^+$ the charge density is so heavily contracted towards the He or F nucleus that no minimum is found in $\rho(r)$ along the internuclear axis. One cannot define a virial hydrogen fragment because the surface, $S(r)$, is collapsed to a line coincident with the internuclear axis. This occurrence is only possible for fragments possessing no core electrons.)
Table 2.1
Partitioning Results\(^a\) for 1st and 2nd Row Diatomic Hydrides\(^b\):

<table>
<thead>
<tr>
<th>AH</th>
<th>(R)</th>
<th>(\bar{C}(A)=\bar{C}(H))</th>
<th>(\hat{u}(A))</th>
<th>(\hat{u}(H))</th>
<th>(\hat{u}_C)</th>
<th>(\hat{u}_{AB})</th>
<th>(\hat{F}_A(A))</th>
<th>(\hat{F}_H(H))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH(X^1\Sigma^+)</td>
<td>3.0150</td>
<td>0.911</td>
<td>-0.001</td>
<td>0.387</td>
<td>-2.747</td>
<td>-2.361</td>
<td>-0.198</td>
<td>-0.101</td>
</tr>
<tr>
<td>BeH(X^2\Sigma^+)</td>
<td>2.5380</td>
<td>0.868</td>
<td>1.520</td>
<td>0.571</td>
<td>-2.203</td>
<td>-0.112</td>
<td>-0.488</td>
<td>-0.116</td>
</tr>
<tr>
<td>BH(X^1\Sigma^+)</td>
<td>2.3360</td>
<td>0.754</td>
<td>1.950</td>
<td>0.493</td>
<td>-1.761</td>
<td>0.682</td>
<td>-0.757</td>
<td>-0.353</td>
</tr>
<tr>
<td>CH(X^2\pi)</td>
<td>2.1240</td>
<td>0.032</td>
<td>0.807</td>
<td>-0.121</td>
<td>-0.068</td>
<td>0.618</td>
<td>0.275</td>
<td>-0.216</td>
</tr>
<tr>
<td>NH(X^3\Sigma^-)</td>
<td>1.9614</td>
<td>-0.323</td>
<td>0.183</td>
<td>-0.176</td>
<td>0.633</td>
<td>0.640</td>
<td>0.986</td>
<td>-0.111</td>
</tr>
<tr>
<td>OH(X^2\pi_i)</td>
<td>1.8342</td>
<td>-0.585</td>
<td>-0.224</td>
<td>-0.148</td>
<td>1.073</td>
<td>0.701</td>
<td>1.774</td>
<td>-0.007</td>
</tr>
<tr>
<td>FH(X^1\Sigma^+)</td>
<td>1.7328</td>
<td>-0.760</td>
<td>-0.449</td>
<td>-0.104</td>
<td>1.317</td>
<td>0.764</td>
<td>2.605</td>
<td>0.084</td>
</tr>
<tr>
<td>NaH(X^1\Sigma^+)</td>
<td>3.5660</td>
<td>0.810</td>
<td>0.017</td>
<td>0.133</td>
<td>-2.890</td>
<td>-2.739</td>
<td>-0.382</td>
<td>-0.067</td>
</tr>
<tr>
<td>MgH(X^2\Sigma^+)</td>
<td>3.2710</td>
<td>0.796</td>
<td>1.701</td>
<td>0.302</td>
<td>-2.602</td>
<td>-0.599</td>
<td>-0.645</td>
<td>-0.139</td>
</tr>
<tr>
<td>AlH(X^1\Sigma^+)</td>
<td>3.1140</td>
<td>0.825</td>
<td>2.274</td>
<td>0.360</td>
<td>-2.568</td>
<td>0.066</td>
<td>-1.145</td>
<td>-0.202</td>
</tr>
<tr>
<td>SiH(X^2\pi)</td>
<td>2.8740</td>
<td>0.795</td>
<td>1.976</td>
<td>0.428</td>
<td>-2.285</td>
<td>0.119</td>
<td>-1.555</td>
<td>-0.281</td>
</tr>
<tr>
<td>PH(X^3\Sigma^-)</td>
<td>2.7080</td>
<td>0.579</td>
<td>1.464</td>
<td>0.317</td>
<td>-1.569</td>
<td>0.212</td>
<td>-1.491</td>
<td>-0.328</td>
</tr>
<tr>
<td>SH(X^2\pi)</td>
<td>2.5510</td>
<td>0.095</td>
<td>0.587</td>
<td>-0.009</td>
<td>0.239</td>
<td>0.339</td>
<td>-0.118</td>
<td>-0.266</td>
</tr>
<tr>
<td>ClH(X^1\Sigma^+)</td>
<td>2.4087</td>
<td>-0.241</td>
<td>-0.006</td>
<td>-0.103</td>
<td>0.581</td>
<td>0.471</td>
<td>1.022</td>
<td>-0.195</td>
</tr>
</tbody>
</table>

\(^a\)All values are expressed in atomic units (au) unless otherwise stated.

\(^b\)All AH wavefunctions are close to the Hartree-Fock limit and were obtained from P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 649 (1967).

\(^c\)\(\bar{C}(\Omega)\) is the net charge of \(\Omega\) and is defined as \(Z_\Omega-N(\Omega)\) where \(Z_\Omega\) is the nuclear charge. \(\Omega\)

\(^d\)A negative value for \(\hat{u}\) implies the direction \(A^+H^-\) for the dipole (1 au = 2.542 D.).

\(^e\)A binding force is positive on \(A\) and negative on \(H\).
Because of its sensitivity to external forces the distribution of charge in (H) of $\text{AH}$ is molded in such a way as to reflect the chemical nature of A. The values of the (H) fragment populations in these molecules closely parallel those that one would expect based on prior knowledge of an electronegativity scale. The transition from electron donor to electron acceptor relative to hydrogen occurs at carbon in the first row and at sulfur in the second row of the periodic table. For both $\text{CH}$ and $\text{SH}$ the H fragment supports a slightly negative net charge. The shift of the transitional member to the right on going down the periodic table is consistent with the arguments stemming from the idea of effective nuclear charge. The field exerted on the valence electrons in S is roughly the same as that exerted on the valence electrons in C. Although the effective nuclear charge is greater in sulfur, the average distance of the valence electrons is also increased from that in carbon.

From the complete study of ground state 1st and 2nd row diatomic hydrides including charged species\(^{(12,27)}\), a relative ordering of the electron withdrawing power of $\text{A}^+$, $\text{A}$ and $\text{A}^-$ with respect to hydrogen can be obtained. The order of decreasing ability to withdraw electrons from H is:

$$\text{F}^+ > \text{O}^+ > \text{F} > \text{N}^+ \sim \text{O} > \text{Cl}^+ > \text{O}^- > \text{N} > \text{C}^+ > \text{Cl} > \text{N}^- > \text{S}^+ > \text{Na}^+ > \text{Li}^+.$$  

The order of increasing ability to donate electrons to $\text{H}$ is:

$$\text{C} < \text{S} < \text{C}^- < \text{S}^- < \text{B}^+ < \text{P}^+ < \text{P} < \text{Al}^+ \sim \text{Mg}^+ < \text{Si}^+ < \text{P}^- < \text{B} < \text{Be}^+ < \text{Si} \sim \text{Mg} < \text{Na} < \text{Al} < \text{Be} < \text{Li} < \text{Si}^-.$$
The (H) fragment when bonded to any member of the first series acquires a positive net charge. All members of the second series donate charge to the (H) fragment in the corresponding diatomic hydride.

Knowledge of the spatial distribution of charge within a fragment is, to some extent, obtained from the fragment multipole moments, particularly the dipole moment. In order to calculate these quantities the choice of an origin must be made. For the monatomic fragment the most natural and convenient location is the nuclear coordinate within the fragment. (Only the dipole moment is discussed in the present chapter. Higher moments are considered in Chapter 5.) By positioning the origin at the nucleus the nuclear charge does not contribute to the fragment dipole moment, \( \tilde{\mu}(\Omega) \). In terms of the electronic charge distribution

\[
\tilde{\mu}(\Omega) = - \int_\Omega \tilde{r} \rho(r) \, dr.
\]  

(2.4)

Note that this definition is valid and unambiguous for any monatomic fragment in any molecular system regardless of the net charges present. For the particular case of a neutral diatomic molecule, AB, the total dipole moment, \( \tilde{\mu}_{AB} \), may be broken down into its fragment components, \( \tilde{\mu}(\Omega) \), plus a charge transfer term, \( \tilde{\mu}_c \). These quantities are related by the expression

\[
\tilde{\mu}_{AB} = \tilde{\mu}(A) + \tilde{\mu}(B) + \tilde{\mu}_c
\]  

(2.5)

where the charge transfer component is expressed as
\( \vec{\mu}_C = \vec{\zeta}(A) \vec{R}_{AB} = -\vec{\zeta}(B) \vec{R}_{AB} \) \hspace{1cm} (2.6)

\( \vec{\zeta}(A) \) is the net charge for the A fragment and \( \vec{R}_{AB} \) is the interatomic distance vector.

In those molecules where bonding is generally considered to be ionic, \( \vec{\mu}(A) \) and \( \vec{\mu}(B) \) are small as the charge distribution about each center is nearly spherical. The molecular dipole moment approaches the value anticipated on the basis of net charges alone. For the diatomic hydrides (Table 2.1) this situation is approached most closely by LiH and NaH and to a lesser extent by HCl, NH, OH and FH. The A fragment in each of these systems is typified by a tight distribution of charge. A sharp increase in the dipole moment of A is exhibited when diffuse unpaired valence density is present. As indicated by the direction of \( \vec{\mu}(A) \) (a negative value for \( \vec{\mu} \) implies the direction \( A^+H^- \) for the dipole moment), the diffuse charge density is accumulated in the non-binding region of \( \text{(A)} \). This build up of charge "behind" A is readily observed in the total molecular charge density maps of BeH, BH (Fig. 2.1), MgH and AlH (Fig. 2.2). For these polar molecules \( \vec{\mu}(A) \) and \( \vec{\mu}_C \) are both large, \( (> 1 \text{ au} \sim 2.5 \text{D}) \) and of the opposite sign so that the total dipole moment does not necessarily reflect the direction of charge transfer. CH and SH represent classic examples of the covalent bond. On bond formation the charge redistribution that takes place is confined, for the most part, to each atomic fragment and very little charge is transferred. This results in fragment dipoles which are intermediate in magnitude between
the ionic and polar systems. The charge transfer component for covalent molecules is small.

Additional information concerning the spatial arrangement of charge within a fragment can be obtained from the electronic force component exerted on the resident nucleus, $\vec{F}_\Omega(\Omega)$. Unlike the dipole moment, the force, because of its $1/r^2$ dependence, is most sensitive to charge polarizations at small $r$. A comparison of the extent to which $\vec{\mu}(A)$ and $\vec{F}_A(A)$ weight the core* and the valence polarizations is clearly illustrated in Table 2.2. It is seen that the fragment dipole is almost entirely a valence effect while it is the core polarizations that dominate the total force on the nucleus. Exceptions to the latter occur in the polar BeH and BH molecules where the build up of charge in the non-binding region** of $(A)$ contributes significantly to the valence component of $\vec{F}_A(A)$.

One of the most important aspects of the Virial Partitioning Theory is its ability to uniquely partition the total energy. Since each fragment of a system obeys the virial relationship during the entire course of a chemical reaction, the virial theorem may be applied separately to energy changes experienced

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*The core region is determined by taking the "best" spherical core loge as defined by loge theory (see footnote on page 26). For the first row atoms these loges closely correspond to the volume of space occupied by 2.00 electrons.

**For diatomic molecules a plane drawn through A perpendicular to the bond axis separates the binding from the non-binding region of $(A)$. 
Table 2.2
Core and Valence Contributions to $\mu^+(A)$ and $F^+_A(A)$ in AH \(^{(d)}\)

<table>
<thead>
<tr>
<th>AH</th>
<th>$R_{\text{core}}$</th>
<th>$\mu_{\text{core}}(A)$ (^{(b)})</th>
<th>$\mu_{\text{val}}(A)$</th>
<th>$F_{A,\text{core}}(A)$ (^{(c)})</th>
<th>$F_{A,\text{val}}(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>1.42</td>
<td>0.015</td>
<td>0.014</td>
<td>-0.199</td>
<td>0.001</td>
</tr>
<tr>
<td>BeH</td>
<td>0.95</td>
<td>-0.003</td>
<td>1.523</td>
<td>-0.112</td>
<td>-0.376</td>
</tr>
<tr>
<td>BH</td>
<td>0.70</td>
<td>-0.000</td>
<td>1.950</td>
<td>0.471</td>
<td>-1.228</td>
</tr>
<tr>
<td>CH</td>
<td>0.53</td>
<td>-0.000</td>
<td>0.807</td>
<td>0.876</td>
<td>-0.601</td>
</tr>
<tr>
<td>NH</td>
<td>0.43</td>
<td>-0.001</td>
<td>0.184</td>
<td>1.357</td>
<td>-0.371</td>
</tr>
<tr>
<td>OH</td>
<td>0.36</td>
<td>-0.000</td>
<td>-0.224</td>
<td>1.923</td>
<td>-0.149</td>
</tr>
<tr>
<td>FH</td>
<td>0.30</td>
<td>-0.000</td>
<td>-0.449</td>
<td>2.533</td>
<td>0.072</td>
</tr>
</tbody>
</table>

\(^{(a)}\) The core radii are taken from the best spherical core logs as defined by loge theory (see footnote on page 26).

\(^{(b)}\) A negative value for $\mu$ implies the direction $A^+H^-$.  

\(^{(c)}\) A negative value for $F_A$ implies an antibinding force on A.  

\(^{(d)}\) All values are in atomic units (see Appendix A2).
by each fragment. For the general fragment $\Omega$ this may be expressed as

$$-2\Delta T(\Omega) = \Delta V'(\Omega) + \Delta V''(\Omega) + \Delta V_n(\Omega)$$  \hspace{1cm} (2.7)$$

where each term represents a change in the fragment energy between two points on a potential surface. For the particular case where the changes correspond to the system being in equilibrium configurations, a virial relation of the form

$$\Delta T(\Omega) = -\Delta E(\Omega)$$  \hspace{1cm} (2.8)$$

applies.* From this equation it is clear that if any total system is to become more stable on going from one equilibrium state to another its kinetic energy must increase. Thus for the formation of a stable chemical bond from separated atoms the total kinetic energy of the system will increase. However, the stability of an isolated fragment within this system might be raised or lowered during the bonding process. Through equation (2.7) any change in fragment stability can be related directly to changes in the individual potential contributions.

In Table 2.3 the total energy changes on bond formation for the ground state diatomic hydrides are recorded. In bond formation, changes in $V''$, the two electron repulsion energy, and

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*In general, LCAO-MO-SCF wave functions, even those close to the Hartree-Fock limit, do not exactly satisfy the Hellmann-Feynman theorem.\(^{31,32}\) Because of the resultant errors in the Hellmann-Feynman forces and hence in $V_n$, equations (2.7) and (2.8) are not rigorously satisfied. Nevertheless, in most cases the errors are small and can be ignored.\(^{11}\)
Table 2.3

Changes in the Total Energies (in au) on Bond Formation for Diatomic Hydrides

<table>
<thead>
<tr>
<th>AH</th>
<th>( \Delta \bar{V} )</th>
<th>( \Delta \bar{V}' )</th>
<th>( \Delta \bar{V}'' )</th>
<th>( \Delta V_\alpha )</th>
<th>( \Delta \bar{T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>-2.2674</td>
<td>1.1592</td>
<td></td>
<td>0.9910</td>
<td>0.0506</td>
</tr>
<tr>
<td>BeH</td>
<td>-3.3002</td>
<td>1.5676</td>
<td></td>
<td>1.5797</td>
<td>0.0764</td>
</tr>
<tr>
<td>NH</td>
<td>-4.3969</td>
<td>2.0672</td>
<td></td>
<td>2.1555</td>
<td>0.0869</td>
</tr>
<tr>
<td>CH</td>
<td>-5.7110</td>
<td>2.7290</td>
<td></td>
<td>2.8493</td>
<td>0.0665</td>
</tr>
<tr>
<td>NH</td>
<td>-7.2063</td>
<td>3.5152</td>
<td></td>
<td>3.5900</td>
<td>0.0455</td>
</tr>
<tr>
<td>OH</td>
<td>-8.9628</td>
<td>4.4381</td>
<td></td>
<td>4.4009</td>
<td>0.0717</td>
</tr>
<tr>
<td>FH</td>
<td>-10.9603</td>
<td>5.4867</td>
<td></td>
<td>5.2370</td>
<td>0.1186</td>
</tr>
<tr>
<td>NaH</td>
<td>-6.5290</td>
<td>3.3583</td>
<td></td>
<td>3.0775</td>
<td>0.0343</td>
</tr>
<tr>
<td>MgH</td>
<td>-7.2720</td>
<td>3.5137</td>
<td></td>
<td>3.6721</td>
<td>0.0424</td>
</tr>
<tr>
<td>AlH</td>
<td>-8.6491</td>
<td>4.2838</td>
<td></td>
<td>4.1746</td>
<td>0.0838</td>
</tr>
<tr>
<td>SiH</td>
<td>-9.9136</td>
<td>4.8622</td>
<td></td>
<td>4.8759</td>
<td>0.0819</td>
</tr>
<tr>
<td>PiH</td>
<td>-11.1951</td>
<td>5.5148</td>
<td></td>
<td>-5.5645</td>
<td>0.0746</td>
</tr>
<tr>
<td>SiH</td>
<td>-12.8170</td>
<td>6.3580</td>
<td></td>
<td>6.2977</td>
<td>0.0960</td>
</tr>
<tr>
<td>ClH</td>
<td>-14.6294</td>
<td>7.0037</td>
<td></td>
<td>7.0734</td>
<td>0.1286</td>
</tr>
</tbody>
</table>
Table 2.4

Energy Partitioning in the 1st and 2nd Row Diatomic Hydrides (a)

<table>
<thead>
<tr>
<th>AH</th>
<th>$\mathcal{T}(A)$</th>
<th>$\mathcal{T}(H)$</th>
<th>$\mathcal{V}'(A)$</th>
<th>$\mathcal{V}'(H)$</th>
<th>$\mathcal{V}''(A)$</th>
<th>$\mathcal{V}''(H)$</th>
<th>$\mathcal{V}_n(A)$</th>
<th>$\mathcal{V}_n(H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>7.3678</td>
<td>0.6235</td>
<td>-17.0893</td>
<td>-3.3726</td>
<td>2.4124</td>
<td>1.0759</td>
<td>-0.0587</td>
<td>1.0497</td>
</tr>
<tr>
<td>BeH</td>
<td>14.3777</td>
<td>0.7717</td>
<td>-33.2401</td>
<td>-4.6957</td>
<td>4.5426</td>
<td>1.5146</td>
<td>-0.0579</td>
<td>1.6376</td>
</tr>
<tr>
<td>BH</td>
<td>24.2289</td>
<td>0.8874</td>
<td>-56.5550</td>
<td>-5.7389</td>
<td>8.0023</td>
<td>1.9035</td>
<td>0.0948</td>
<td>2.0607</td>
</tr>
<tr>
<td>CH</td>
<td>37.6324</td>
<td>0.6226</td>
<td>-90.9057</td>
<td>-3.9409</td>
<td>14.1670</td>
<td>1.5204</td>
<td>1.4740</td>
<td>1.3753</td>
</tr>
<tr>
<td>NH</td>
<td>54.4536</td>
<td>0.4935</td>
<td>-133.4897</td>
<td>-3.0683</td>
<td>22.0258</td>
<td>1.0328</td>
<td>2.5568</td>
<td>1.0431</td>
</tr>
<tr>
<td>OH</td>
<td>75.0150</td>
<td>0.3665</td>
<td>-185.8531</td>
<td>-2.2035</td>
<td>32.1466</td>
<td>0.7462</td>
<td>3.6766</td>
<td>0.7243</td>
</tr>
<tr>
<td>FH</td>
<td>99.7725</td>
<td>0.2547</td>
<td>-249.1576</td>
<td>-1.4671</td>
<td>44.8396</td>
<td>0.4938</td>
<td>4.7730</td>
<td>0.4640</td>
</tr>
<tr>
<td>NaH</td>
<td>161.8264</td>
<td>0.5736</td>
<td>-390.4717</td>
<td>-6.7776</td>
<td>66.5279</td>
<td>2.8440</td>
<td>0.2909</td>
<td>2.7866</td>
</tr>
<tr>
<td>MgH</td>
<td>199.5042</td>
<td>0.6489</td>
<td>-479.2303</td>
<td>-8.0763</td>
<td>79.9716</td>
<td>3.3567</td>
<td>0.2503</td>
<td>3.4218</td>
</tr>
<tr>
<td>AlH</td>
<td>241.7229</td>
<td>0.7406</td>
<td>-578.7089</td>
<td>-9.4225</td>
<td>95.1105</td>
<td>3.9193</td>
<td>0.1526</td>
<td>4.0220</td>
</tr>
<tr>
<td>SiH</td>
<td>288.6282</td>
<td>0.8034</td>
<td>-689.5592</td>
<td>-10.7479</td>
<td>112.0727</td>
<td>4.4953</td>
<td>0.2301</td>
<td>4.6458</td>
</tr>
<tr>
<td>PH</td>
<td>340.4873</td>
<td>0.7805</td>
<td>-813.6910</td>
<td>-10.7023</td>
<td>131.7975</td>
<td>4.4956</td>
<td>0.9189</td>
<td>4.6456</td>
</tr>
<tr>
<td>SH</td>
<td>397.4594</td>
<td>0.6165</td>
<td>-952.7586</td>
<td>-7.9278</td>
<td>154.9379</td>
<td>3.2990</td>
<td>2.9019</td>
<td>3.3958</td>
</tr>
<tr>
<td>ClH</td>
<td>459.6009</td>
<td>0.4938</td>
<td>-1103.9825</td>
<td>-5.9381</td>
<td>180.2272</td>
<td>2.4757</td>
<td>4.5535</td>
<td>2.5199</td>
</tr>
</tbody>
</table>

(a) All values are in atomic units (see Appendix A2).
Table 2.5

Changes in Fragment Energies on Bond Formation for Diatomic Hydrides (a)

<table>
<thead>
<tr>
<th>AH</th>
<th>ΔT(A)</th>
<th>ΔT(H)</th>
<th>ΔV'(A)</th>
<th>ΔV'(H)</th>
<th>ΔV''(A)</th>
<th>ΔV''(H)</th>
<th>ΔV_n(A)</th>
<th>ΔV_n(H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>-0.0649</td>
<td>0.1235</td>
<td>0.0571</td>
<td>-2.3245</td>
<td>0.1314</td>
<td>1.0278</td>
<td>-0.0587</td>
<td>1.0497</td>
</tr>
<tr>
<td>BeH</td>
<td>-0.1953</td>
<td>0.2717</td>
<td>0.3954</td>
<td>-3.6956</td>
<td>0.0530</td>
<td>1.5146</td>
<td>-0.0579</td>
<td>1.6376</td>
</tr>
<tr>
<td>BH</td>
<td>-0.3005</td>
<td>0.3874</td>
<td>0.3424</td>
<td>-4.7393</td>
<td>0.1634</td>
<td>1.9038</td>
<td>0.0948</td>
<td>2.0607</td>
</tr>
<tr>
<td>CH</td>
<td>-0.0560</td>
<td>0.1225</td>
<td>-2.7699</td>
<td>-2.9411</td>
<td>1.4081</td>
<td>1.3209</td>
<td>1.4740</td>
<td>1.3753</td>
</tr>
<tr>
<td>NH</td>
<td>0.0520</td>
<td>-0.0065</td>
<td>-5.1377</td>
<td>-2.0691</td>
<td>2.4762</td>
<td>1.0390</td>
<td>2.5568</td>
<td>1.0431</td>
</tr>
<tr>
<td>OH</td>
<td>0.2055</td>
<td>-0.1338</td>
<td>-7.7788</td>
<td>-1.2040</td>
<td>3.6908</td>
<td>0.7473</td>
<td>3.6766</td>
<td>0.7243</td>
</tr>
<tr>
<td>FH</td>
<td>0.3639</td>
<td>-0.2453</td>
<td>-10.4919</td>
<td>-0.4684</td>
<td>4.9916</td>
<td>0.4951</td>
<td>4.7730</td>
<td>0.4640</td>
</tr>
<tr>
<td>NaH</td>
<td>-0.0393</td>
<td>0.0736</td>
<td>-0.7514</td>
<td>-5.7776</td>
<td>0.5143</td>
<td>2.8440</td>
<td>0.2909</td>
<td>2.7866</td>
</tr>
<tr>
<td>MgH</td>
<td>-0.1066</td>
<td>0.1489</td>
<td>-0.1957</td>
<td>-7.0763</td>
<td>0.1570</td>
<td>3.3567</td>
<td>0.2503</td>
<td>3.4218</td>
</tr>
<tr>
<td>AlH</td>
<td>-0.1566</td>
<td>0.2406</td>
<td>-0.2263</td>
<td>-8.4225</td>
<td>0.3642</td>
<td>3.9196</td>
<td>0.1526</td>
<td>4.0220</td>
</tr>
<tr>
<td>SiH</td>
<td>-0.2214</td>
<td>0.3034</td>
<td>-0.1657</td>
<td>-9.7479</td>
<td>0.3669</td>
<td>4.4953</td>
<td>0.2301</td>
<td>4.6458</td>
</tr>
<tr>
<td>PH</td>
<td>-0.2060</td>
<td>0.2805</td>
<td>-1.4928</td>
<td>-9.7023</td>
<td>1.0192</td>
<td>4.4956</td>
<td>0.9189</td>
<td>4.6456</td>
</tr>
<tr>
<td>SH</td>
<td>-0.0196</td>
<td>0.1165</td>
<td>-5.8892</td>
<td>-6.9278</td>
<td>3.0590</td>
<td>3.2990</td>
<td>2.9019</td>
<td>3.3958</td>
</tr>
<tr>
<td>ClH</td>
<td>+0.1348</td>
<td>-0.0062</td>
<td>-9.6463</td>
<td>-4.9831</td>
<td>4.8487</td>
<td>2.4757</td>
<td>4.5535</td>
<td>2.5199</td>
</tr>
</tbody>
</table>

(a) All values are in atomic units (see Appendix A2).
and in $\nu_n$, the nuclear repulsions, are greater than zero. Hence, stabilization occurs only by virtue of a decrease in $\nu'$, the electron-nuclear attractions.

Table 2.4 contains the energy partitioning results for the hydride series while Table 2.5 summarizes the changes associated with bond formation. The molecules LiH to CH of the 1st row and NaH to SH of the 2nd row in the periodic table are all characterized by a destabilization (relative to the free atom) of the A fragment. A glance at Table 2.1 reveals that these same molecules are just those in which charge is transferred from the A to the H fragment. Thus binding in these molecules arises from the charge transferred to and the subsequent stabilization of the H fragment. It is to be noted, though, that the fragment total energy is not a simple function of the fragment population. The maximum stability of (A) and instability of (H) occur for BH and SiH in the 1st and 2nd rows respectively while the maximum transfer of charge takes place in the LiH and AlH molecules.

In those molecules where there is significant charge transfer in the direction (A) → (H), $\Delta \nu'(A)$, $\Delta \nu''(A)$ and $\Delta \nu_n(A)$ are all positive and destabilizing. The total energy of the H fragment is greatly reduced because of increased contributions to $\nu'(H)$ from the additional charge gained by the fragment. A clue to the rationale of charge transfer in these systems is found upon closer examination of the one-electron potential energy, $\Delta \nu'_A(A)$, the attraction of the A nucleus to the charge density in (A), is large and positive owing to the charge lost by (A). In contrast, $\Delta \nu'_A(H)$, the attraction of the A nucleus to the charge in (H), is
large and negative. The net result is that the attraction of the A nucleus with the charge transferred to (H) is comparable to or greater than the attraction with the same charge density centered on A in the atomic state. The large magnitude of $V'_A(H)$ is a result of the very pronounced polarizations of the density in (H) toward (A); a fact attested to by the large positive dipole moment in (H) for these systems.

The transitional members of the hydride series, CH and SH, are covalent molecules with only slight transfer of charge to (H). In both cases the H fragment accounts for the overall stability. The interesting feature concerning the binding in these species is the extent to which the energy changes approach the limiting case of binding in a homonuclear diatomic molecule; i.e., in spite of the differences in their population, the changes in each of the potential interactions for the A and H fragments are approximately the same. This limiting behavior is approached most closely by CH since the charge transfer in SH is nearly three times that of the former. The energy changes in these systems result primarily from the redistribution of charge within each fragment. The most prominent of these changes stems from the stabilizing interactions of each nucleus with the charge density in the adjacent fragment, $V'_A(A')$. For both CH and SH the change in $V'_A(H)$ is roughly equal to the change in $V'_H(A)$ while for the members discussed previously $|\Delta V'_A(A)| \approx 2 |\Delta V'_H(A)|$.

The remaining hydrides, CH, NH, OH and FH, are those for which there is an increasing degree of charge transfer from (H). It is the A fragment which constitutes the source of stability
in these systems. A large contributor to the energy lowering of \((A)\) comes from \(V'(A)\) which in turn is dominated by \(V_A'(A)\), a quantity that decreases steadily with increasing fragment population. The major interaction is the attraction of the charge in \((A)\) with the proton, \(V_H'(A)\). In these molecules the value of \(V_H'(A)\) is enhanced by polarizations of the charge density in \((A)\) toward \(H\). The signs and magnitudes of \(\hat{u}(A)\) and \(\hat{F}_A(A)\) (Table 2.1) support the observed trend in \(V_H'(A)\).

The behaviour of the nuclear virial for a fragment deserves some comment. The quantity \(V_n(\alpha)\) corresponds to the fraction of the total nuclear repulsive potential experienced by the fragment \((\alpha)\). For the diatomic \(AH\) molecule the nuclear virial for the \(A\) fragment is equal to the sum of the virials of the forces exerted on both the \(A\) and \(H\) nuclei by the charge density in \((A)\). A mathematical statement of \(V_n(A)\) is given by

\[
V_n(A) = \overrightarrow{R}_A \cdot \overrightarrow{F}_A(A) + \overrightarrow{R}_H \cdot \overrightarrow{F}_H(A)
\]

where \(\overrightarrow{R}_A\) and \(\overrightarrow{R}_H\) are measured from an origin which is generally in the vicinity of \(R_{AB}/2\), the bond mid-point\(^{11}\).

The force exerted on a nucleus may either be binding (if the force tends to decrease the \(A-H\) internuclear distance) or antibinding. A binding force gives a positive contribution to \(V_n\); an antibinding force gives a negative contribution. Since the force exerted on the nuclei by the charge density in various spatial regions is characteristic of the binding in the system\(^{29,30}\), the partitioning of the nuclear potential is similarly characteristic of the nature of the charge distribution within a fragment. In
the ionic molecules of LiH and NaH the charge distribution in the A fragment \((A = \text{Li or Na})\) is polarized in a direction counter to the direction of charge transfer, that is, polarized in the direction so as to create an antibinding force on the A nucleus. This results in a negative contribution from the term \(\mathbf{R}_A \cdot \mathbf{F}_A(A)\) and a proportionately small value for \(\nabla_n(A)\). In fact, \(\nabla_n(\text{Li})\) is slightly negative.

The molecules BeH and BH of the first-row and MgH, AlH, SiH and PH of the second-row are characterized by the localization of unshared valence density in the non-binding region of \((A)\). Thus in these systems \(\mathbf{F}_A(A)\) is again antibinding and large in magnitude. As the charge in the hydrogen fragments is polarized into the bond the value of \(\nabla_n(H)\) is considerably greater than \(\nabla_n(A)\) for ionic molecules.

The charge distributions in both fragments of CH are polarized into the bond. All four force contributions, \(\mathbf{F}_C(C), \mathbf{F}_C(H), \mathbf{F}_H(C)\) and \(\mathbf{F}_H(H)\) are binding and their virials add for each fragment. The homopolar nature of this molecule is reflected in an almost equal sharing of \(\nabla_n\) between the two fragments. In SH, the transitional member of the second row of the periodic table, \(\mathbf{F}_S(S)\) is small and antibinding while the remaining force contributions are all binding. The result is a slightly unbalanced sharing of \(\nabla_n\) with the H fragment having the greater proportion.

The sharp rise in the values of \(\nabla_n(A)\) for the molecules HCl, NH, OH and HF is due in part to an increasing A fragment population but is also due to increased polarizations of charge into the binding region of the fragment.
The fact that an antibinding force gives a negative contribution to $\mathbf{V}_n(A)$ is an important point. It explains how polarizations of the charge density into non-bonded regions of space are energetically not only feasible, but favourable. Polarization of charge into a non-bonding region of a fragment (A) necessarily reduces the magnitude of its interaction with the neighbouring nucleus B, the interaction $\mathbf{V}_B(A)$. The same polarization, however, yields a negative contribution to $\mathbf{V}_n(A)$. Thus the localization of charge density in non-bonding regions of space is understandable as it leads to a local lowering of the energy via the nuclear virial contribution to the total energy of the system.

Before leaving the diatomic hydrides, it is noteworthy to look at one further aspect of virial partitioning as it applies to the hydrogen fragment. As was mentioned in Section (A) of this chapter, virial fragments maximize the retention of information carried by the charge density in different environments. It has been amply shown that the characterization of the H fragment, when bonded to different (A)'s, varies rather dramatically. If, on the other hand, (H) is bonded to the same (A) in different systems a remarkable constancy of (H) fragment identity is achieved. These observations are based on a comparative study of (H) in a number of AH and $\text{AH}_n$ systems ($A = \text{Be, B, C, N and O}$). The results are summarized in Table 2.6.

The similarity of the three-dimensional electronic charge density within the H fragment in any of the corresponding AH + $\text{AH}_n$ pairs (charge density maps for AH appear in Figure 2.1; maps for
<table>
<thead>
<tr>
<th></th>
<th>$\bar{N}(H)$</th>
<th>$\Delta N(H)$</th>
<th>$\bar{T}(H)$</th>
<th>$\Delta T(H)$</th>
<th>$\bar{V}'(H)$</th>
<th>$\Delta V'(H)$</th>
<th>$\bar{V}''(H)$</th>
<th>$\Delta V''(H)$</th>
<th>$\bar{V}_n(H)$</th>
<th>$\Delta V_n(H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeH</td>
<td>1.868</td>
<td>0.007</td>
<td>0.772</td>
<td>0.012</td>
<td>-4.696</td>
<td>0.357</td>
<td>1.515</td>
<td>-0.185</td>
<td>1.638</td>
<td>-0.195</td>
</tr>
<tr>
<td>BeH$_2$</td>
<td>1.861</td>
<td></td>
<td>0.760</td>
<td>0.012</td>
<td>-5.053</td>
<td></td>
<td>1.700</td>
<td></td>
<td>1.833</td>
<td></td>
</tr>
<tr>
<td>BH</td>
<td>1.754</td>
<td>0.042</td>
<td>0.888</td>
<td>0.012</td>
<td>-5.739</td>
<td>0.895</td>
<td>1.904</td>
<td>-0.487</td>
<td>2.061</td>
<td>-0.430</td>
</tr>
<tr>
<td>BH$_5$</td>
<td>1.712</td>
<td></td>
<td>0.876</td>
<td>0.012</td>
<td>-6.634</td>
<td></td>
<td>2.391</td>
<td></td>
<td>2.491</td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>1.032</td>
<td>-0.032</td>
<td>0.622</td>
<td>-0.024</td>
<td>-3.941</td>
<td>1.168</td>
<td>1.321</td>
<td>-0.579</td>
<td>1.375</td>
<td>-0.542</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.062</td>
<td></td>
<td>0.646</td>
<td>-0.024</td>
<td>-5.109</td>
<td></td>
<td>1.900</td>
<td></td>
<td>1.917</td>
<td></td>
</tr>
<tr>
<td>NH</td>
<td>0.677</td>
<td>0.041</td>
<td>0.493</td>
<td>0.012</td>
<td>-3.070</td>
<td>0.272</td>
<td>1.041</td>
<td>-0.161</td>
<td>1.043</td>
<td>-0.136</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.636</td>
<td></td>
<td>0.481</td>
<td>0.012</td>
<td>-3.342</td>
<td></td>
<td>1.202</td>
<td></td>
<td>1.179</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>0.415</td>
<td>0.021</td>
<td>0.366</td>
<td>0.014</td>
<td>-2.206</td>
<td>0.024</td>
<td>0.749</td>
<td>-0.031</td>
<td>0.724</td>
<td>-0.021</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.394</td>
<td></td>
<td>0.352</td>
<td>0.014</td>
<td>-0.230</td>
<td></td>
<td>0.780</td>
<td></td>
<td>0.745</td>
<td></td>
</tr>
</tbody>
</table>

(a) All values are in atomic units (see Appendix A2)
$A_{H\gamma}$ are found in Fig. 4.1) is evidenced by the small differences in population of (H) between these pairs of molecules. Further, changes in the kinetic energy and hence the total energy of the $H$ fragment vary by no more than 9 kcal/mole. This constancy in $\rho(x)$, $N(H)$ and $T(H)$ is found in spite of relatively large changes in the individual forces exerted on (H) on going from $AH$ to $AH_n$. For example, the change in the electron-nuclear attractive potential within the $H$ fragment on passing from $CH$ to $CH_4$ is -733 kcal/mole. Similarly the virial of the nuclear forces increases by the amount of 340 kcal/mole during the same process. However, the sum of the nuclear-virial and electron-electron repulsions is of almost equal magnitude but of opposite sign to the change in the $V'(H)$ contribution and hence the net change in the total virial is relatively small.

The reader is asked to recall an earlier discussion where it was stated that a fragment (Ω) will be identical in two systems if its outer virial, $\nu^O(\Omega)$, is identical in the two systems. The only pair of molecules for which the outer virials have been calculated explicitly* is the $BeH \leftrightarrow BeH_2$ pair. In $BeH$ the virial of the forces exerted on (H) by (Be), i.e., the outer virial of (H), is -0.7174 au. A similar calculation for the $H$ fragment in $BeH_2$ yields a value for $\nu^O(H)$ of -0.7196 au; a difference of about 2 kcal/mole. Thus the virial definition of a fragment does indeed account for the preservation of the hydrogen identity in this system.

*The problem lies with the calculation of $V''_H(H)$. To obtain this value a time-consuming six-dimensional numerical integration is required.
(ii) The Cyano Fragment

Virial partitioning is not restricted to fragments containing one nuclear center. The only requirement of a virial fragment is that it be bounded by one or more surfaces of zero flux. Any polyatomic fragment may, of course, be further partitioned into its monatomic fragment components.

Partitioning results for the CN fragment together with those of its (C) and (N) constituents are presented in Table 2.7. As seen from the population data, the CN fragment can function both as an electron donor, as is the case in the systems ClCN, OCN⁻ and FCN, and an electron acceptor, as is the case in the HCCCN, HCN, CH₃CN and SCN⁻ systems.

In all of the molecular systems studied (CN) is characterized by a large transfer of charge from (C) to (N). In every case the N fragment maintains a net negative charge greater than 1 e⁻ while the net charge on the C fragment is, in most cases, in excess of +1 e⁻ and, for FCN and OCN⁻ in particular, is in excess of +2 e⁻.

The C and N fragment populations given here differ significantly from those calculated from any of the many models based on orbital population analysis.* Orbital based schemes for determining populations suffer from a number of inherent shortcomings. Firstly, the populations are basis set dependent.

*The most common of the orbital based population schemes is that proposed by Mulliken[33]. In this scheme an atomic population is composed of "localized contributions" (calculated from atomic orbitals, AO's, associated with a given center) and "overlap contributions" (calculated from orbital overlaps with AO's on the
Table 2.7

Partitioning Results for the CN Fragment in Different Molecular Systems

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Reference</th>
<th>$\bar{C}(CN)$</th>
<th>$\bar{C}(C)$</th>
<th>$\bar{C}(N)$</th>
<th>$\Delta E(CN)^a$</th>
<th>$\Delta E(C)$</th>
<th>$\Delta E(N)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>b</td>
<td>0.000</td>
<td>1.123</td>
<td>-1.123</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>c</td>
<td>-1.070</td>
<td>0.374</td>
<td>-1.444</td>
<td>-0.453</td>
<td>-0.503</td>
<td>0.050</td>
</tr>
<tr>
<td>CN⁻</td>
<td>b</td>
<td>-1.000</td>
<td>0.740</td>
<td>-1.740</td>
<td>-0.352</td>
<td>0.013</td>
<td>-0.365</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>d</td>
<td>-0.340</td>
<td>1.104</td>
<td>-1.444</td>
<td>-0.308</td>
<td>-0.036</td>
<td>-0.272</td>
</tr>
<tr>
<td>HCN</td>
<td>c</td>
<td>-0.152</td>
<td>1.284</td>
<td>-1.436</td>
<td>-0.364</td>
<td>0.013</td>
<td>-0.377</td>
</tr>
<tr>
<td>HCCCN</td>
<td>c</td>
<td>-0.100</td>
<td>1.013</td>
<td>-1.113</td>
<td>-0.120</td>
<td>-0.175</td>
<td>0.055</td>
</tr>
<tr>
<td>NCCN</td>
<td>c</td>
<td>0.000</td>
<td>1.222</td>
<td>-1.222</td>
<td>-0.062</td>
<td>0.018</td>
<td>-0.080</td>
</tr>
<tr>
<td>CICN</td>
<td>c</td>
<td>0.003</td>
<td>1.296</td>
<td>-1.293</td>
<td>0.018</td>
<td>0.099</td>
<td>-0.082</td>
</tr>
<tr>
<td>OCN⁻</td>
<td>c</td>
<td>0.514</td>
<td>2.139</td>
<td>-1.625</td>
<td>0.517</td>
<td>0.545</td>
<td>-0.027</td>
</tr>
<tr>
<td>FCN</td>
<td>c</td>
<td>0.750</td>
<td>2.012</td>
<td>-1.262</td>
<td>0.502</td>
<td>0.555</td>
<td>-0.053</td>
</tr>
</tbody>
</table>

$^a\Delta E(\Omega)$ denotes changes in the fragment energy relative to the corresponding energy in the reference CN molecule. A negative value for $\Delta E(\Omega)$ implies a decrease in energy relative to that in CN.

For CN: $E(CN) = -92.084$ au, $E(C) = -37.152$ au, $E(N) = -54.932$ au.

$^b$Wavefunctions from P. E. Cade and W. Huo, ref. 35.

$^c$Wavefunctions from A. D. McLean and M. Yoshimine, ref. 36.

$^d$Wavefunction from R. F. W. Bader and A. J. Duke, ref. 11.
Figure 2.3

Contour maps\textsuperscript{a} of the electronic charge densities together with the virial partitioning surfaces for systems containing the cyano group.

Plot A; CN
Plot B; CN\textsuperscript{−}
Plot C; F-CN
Plot D; H-CN

\textsuperscript{a}For contour values see caption for Figure 2.1.
Figure 2.4

Contour maps\(^a\) of the electronic charge densities together with the virial partitioning surfaces for systems containing the cyano group.

Plot A; NCCN
Plot B; OCN
Plot C; SCN
Plot D; ClCN

\(^a\)For contour values see caption for Figure 2.1.
For a given molecule, wavefunctions which are of equal accuracy and which predict similar distributions of charge but which employ different orbital basis sets can yield quite different populations\(^{(34)}\). Secondly, the populations do not refer to any well-defined region of space since the orbitals assigned to a given atomic center extend over all space. Thus, one does not necessarily expect to find any agreement between a population determined by the integration of the charge density over a well-defined region of physical space, and an orbital based population defined in terms of a many-dimensional mathematical function space.

Consider the population data in context with the spatial distribution of the virial fragment. Plots of the charge distributions together with the zero-flux surfaces for the series of linear cyano compounds are shown in Figures 2.3 and 2.4. In addition, plots for HCCCN and CH\(_3\)CN are found in Figures 2.5 and 3.2 respectively. The two molecular systems in which the C fragment is most depleted of its electronic charge, FCN and its isoelectronic analogue, OCN\(^-\), are the two systems in which the spatial domain of (C) is reduced to the largest extent to a thin, wedge-like shape, sandwiched between two terminal fragments. In SCN\(^-\), where (C) attains its largest population, the volume of (C) is expanded relative to that in either OCN\(^-\) remaining centers). A serious weakness in the method, apart from those mentioned above, lies with the overlap term which must be partitioned in some manner between the two centers involved. Mulliken suggested that the overlap contributions be partitioned equally, but clearly, any choice of division is artificial from a chemical point of view.
Notice that the changes in the charge distribution within the C fragment are primarily confined to the "R" side of the RCN molecule and that \( \rho(r) \) in the nitrogen side as well as in the N fragment itself remains relatively unchanged by the effect of different R fragments. A quantitative measure of the changes of \( \rho(r) \) in the binding region between C and N is given by the relative changes in the position of the internuclear null point in this region. From the data in Table 2.8, in which \( R_{CN} \) represents the C-N internuclear distance and \( n_N \) denotes the distance from N to the null point, it is seen that the relative position of the null point, given by the ratio \( n_N/R_{CN} \), is remarkably constant.

The observed similarity of the charge distribution within \( (N) \) is reflected by a smaller variation in the properties of this fragment as compared to the C fragment. While the population of the C fragment varies by more than 1.7 electrons in the molecules listed in Table 2.7, the population of \( (N) \) changes by only 0.5 e\(^-\), or less than one-third of the variation in \( (C) \). Similarly the maximum change the total energy of \( (N) \), a property which is a more sensitive indicator to changes in the charge distribution, is 0.43 au as compared to changes of 1.058 au and 0.970 au in the carbon and cyano fragments, respectively.

The carbon fragment in CN, therefore, acts as a "buffer" to changes the external fields generated by various R fragments in RCN type molecular systems. Although the properties of the
Table 2.8

The Relative Position of the C-N Internuclear Null Point
in a Series of Molecular Systems

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( R_{CN} ) (au)</th>
<th>( n_N/R_{CN} )</th>
<th>Molecule</th>
<th>( R_{CN} ) (au)</th>
<th>( n_N/R_{CN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>2.214</td>
<td>0.655</td>
<td>HCCCCN</td>
<td>2.186</td>
<td>0.638</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>2.300</td>
<td>0.639</td>
<td>NCCCN</td>
<td>2.186</td>
<td>0.656</td>
</tr>
<tr>
<td>CN⁻</td>
<td>2.214</td>
<td>0.654</td>
<td>ClCN</td>
<td>2.198</td>
<td>0.655</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>2.154</td>
<td>0.658</td>
<td>OCN⁻</td>
<td>2.281</td>
<td>0.638</td>
</tr>
<tr>
<td>HCN</td>
<td>2.109</td>
<td>0.656</td>
<td>FCN</td>
<td>2.202</td>
<td>0.657</td>
</tr>
</tbody>
</table>

\( R_{CN} \) is the Carbon-Nitrogen interatomic distance.

\( n_N \) is the distance (au) from N to the null point.
cyano fragment as a whole change significantly between these systems, the changes are predominantly a result of changes in \( \rho(r) \) which take place in that part of the C fragment contained in the R-C binding region. The charge distribution in the C-N binding region as well as that in the N fragment is affected to a lesser extent by the nature of the R fragment. Thus, it is a consequence of the "buffering effect" of (C) that the N fragment of the cyano group can maintain a characteristic set of properties in different molecular systems.

(iii) **Acetylene and its Monosubstituted Derivatives**

Properties associated with four monosubstituted derivatives of acetylene (LiCCH, FCCH, ClCCH and NCCCH) are compared and discussed with reference to acetylene, HCCH, in terms of features of the charge distributions characterizing these molecules. Comparisons are also made between the CCH and CN fragments which are isoelectronic and similar in the sense that the N of CN is a united atom combination of C + H in CCH.

The results of partitioning are collected in Table 2.9, where fragment properties of (CCH) and its monatomic components are given. The acetylenic carbons in the molecules listed are identified as either \( \text{C}_\alpha \) or \( \text{C}_\beta \), depending on whether the corresponding fragment is adjacent to or once removed from the site of substitution. Contour plots of the charge distributions showing the partitioning surfaces are illustrated in Figure 2.5.

The CCH fragment, like the CN fragment, can act as both an electron donor or acceptor. The donor/acceptor powers of
### Table 2.9

Partitioning Results for the CCH Fragment in Acetylene and its Monosubstituted Derivatives

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\zeta$(CCH)</th>
<th>$\zeta$(C&lt;sub&gt;a&lt;/sub&gt;)</th>
<th>$\zeta$(C&lt;sub&gt;b&lt;/sub&gt;)</th>
<th>$\zeta$(H)</th>
<th>$\Delta \zeta$(CCH)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$\Delta \zeta$(C&lt;sub&gt;a&lt;/sub&gt;)</th>
<th>$\Delta \zeta$(C&lt;sub&gt;b&lt;/sub&gt;)</th>
<th>$\Delta \zeta$(H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCCH</td>
<td>-0.142</td>
<td>-0.142</td>
<td>-0.142</td>
<td>0.142</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>LiCCH</td>
<td>-0.927</td>
<td>-0.112</td>
<td>-0.898</td>
<td>0.093</td>
<td>-0.309</td>
<td>0.235</td>
<td>-0.523</td>
<td>-0.021</td>
</tr>
<tr>
<td>FCCH</td>
<td>0.765</td>
<td>0.167</td>
<td>0.441</td>
<td>0.156</td>
<td>0.510</td>
<td>0.152</td>
<td>0.355</td>
<td>0.003</td>
</tr>
<tr>
<td>ClCCH</td>
<td>0.091</td>
<td>-0.247</td>
<td>0.225</td>
<td>0.140</td>
<td>0.093</td>
<td>-0.121</td>
<td>0.220</td>
<td>-0.006</td>
</tr>
<tr>
<td>NCCCH</td>
<td>0.100</td>
<td>-0.018</td>
<td>-0.037</td>
<td>0.156</td>
<td>-0.024</td>
<td>-0.034</td>
<td>0.015</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

<sup>a</sup> Wavefunctions are those of A. D. McLean and M. Yoshimine, ref. 36. For each molecule the wavefunction corresponding to the lowest energy was used.

<sup>b</sup> $\Delta \zeta(\Omega)$ denotes changes in the fragment energy relative to the corresponding energy in the reference HCCH molecule. A negative value for $\Delta \zeta(\Omega)$ implies a decrease in energy relative to that in HCCH.

For HCCH: $E$(CCH) = -76.142 au, $E$(C<sub>a</sub>) = $E$(C<sub>b</sub>) = -37.795 au, $E$(H) = -0.552 au.
Figure 2.5

Contour maps\(^a\) of the electronic charge densities together with the virial partitioning surfaces for mono-substituted acetylenes.

Plot A; HCCH
Plot B; HCCl
Plot C; HCCF
Plot D; HCCLi
Plot E; HCCCN

\(^a\)For contour values see caption for Figure 2.1.
both (CCH) and (CN) are similar as is evidenced in the following list in which the net charge of the CCH fragment for the molecule indicated is followed, in brackets, by the net charge on CN in the corresponding cyano compound: HCCCH, -0.142 (-0.152); FCCH, 0.765 (0.750); CICCH, 0.091 (0.003); NCCCH, 0.100 (0.000).

Recall that in the cyano group the (C) served to "buffer" the N fragment from the effects of substitution. If one considers the terminal CH fragment in CCH that is the fragment analogous to (N) in CN, it is apparent from Table 2.8 (by combining the results of the C_B and H fragments) that the properties of (CH) are quite sensitive to the nature of the substituent fragment and that a buffering effect similar to that which takes place in CN does not occur in CCH.

The properties of (H) in (CCH) do, however, exhibit a high degree of constancy in the molecules studied. (The retention of the H fragment identity is reflected in the plots of Figure 5.2 by the fact that the density contours describing the charge distribution within (H) are nearly superimposable on one another.) The proton in each of the acetylenes is acidic in character, having a net charge which varies only slightly from +0.142 to its value in HCCCH.

Of the two acetylenic carbon fragments it is (C_B), the fragment once removed from the site of substitution, which incurs the largest changes from the effects of substitution. In LiCCH, where 0.927 electrons are transferred to (CCH), the population
of \((C_B)\) is increased by 0.756 \(e^-\) relative to its corresponding value in HCCH. By comparison, the population of \((C_\alpha)\) has actually decreased by 0.030 \(e^-\). In FCCH, where there is a charge transfer of 0.765 \(e^-\) to \((F)\), it is again the \(C_B\) fragment which experiences the largest change in population \((C(C_B) = 0.441 \, e^-\) whereas \(C(C_\alpha) = 0.167 \, e^-\)).

The pattern of population changes in the carbon fragments of LiCCH and FCCH as well as those in the other acetylene derivatives are closely coupled with a shifting of the zero-flux surface common to both C fragments. In HCCH, symmetry dictates a planar partitioning surface separating the carbon fragments. In the mono-substituted derivatives the shape of the corresponding surface, being no longer constrained by symmetry, is determined by the redistribution of charge accompanying the substitution.

By replacing the \((H)\) in HCCH with the electropositive Li fragment, it is apparent from the density plot for LiCCH in Figure 2.5 that there is a reorganization of charge density causing the surface common to the two C fragments to shift from the bond midpoint (its location in HCCH) toward the \(C_\alpha\) nucleus. In contrast, the CCH fragment when bonded to the electronegative \(F\) fragment undergoes a charge reorganization which is reflected by the shift of the surface (between the carbon centers) toward the \(C_B\) nucleus.

The calculated population changes in \((C_\alpha)\) and \((C_B)\) correlate with the observed shifts in their common surface. For
example, in LiCCH the larger population of \((C_B)\) is due, in part, to the shift in \(S(r)\) toward \(C_\alpha\) which accompanies a transfer of charge in the opposite direction, i.e. into the \(C_B\) fragment.

In summary, the CCH fragment in the general molecule RCCH can exhibit, as can the isoelectronic CN fragment in the corresponding cyano compound, a wide range of properties depending on the chemical nature of \((R)\). However, the effect of the \(R\) fragment on the charge distributions within \((CCH)\) and \((CN)\) differ distinctively. In RCN the effect of the substituent is felt predominantly by \((C)\), the fragment adjacent to the site of substitution. In contrast, the changes which take place in the acetylenic fragment are, to a large extent, localized to the \(C_B\) fragment.
CHAPTER 3
PARTITIONING OF TWO $S_N^2$ REACTIONS

(A) Introductory Remarks

A detailed study of the energy changes and redistribution of charge of two bimolecular nucleophilic displacement ($S_N^2$) reactions is undertaken in this chapter. The $S_N^2$ reaction, a reaction of general importance to organic chemistry, may be represented by

$$N + \overset{\text{C-L}}{\text{[transition state]}} \rightarrow N-C + L$$

where $N$ is the nucleophile and $L$ is the leaving group. The transition state corresponds to the highest point on the lowest energy profile between the reactants and products. The carbon atom at which substitution occurs undergoes inversion of its configuration because the nucleophile approaches along a line diametrically opposite to the bond to the leaving group.

Ab initio studies of these reactions are, at present, limited to the gas phase. (This is primarily due to the large amount of computer time necessary to obtain reliable results.) In contrast, investigations at the experimental level have been, for the most part, confined to reactions in solution. In the latter systems the solvent plays an important role in both the thermodynamics and kinetics of the $S_N^2$ process and, hence, a direct comparison of experiment and theory has not been possible. Happily, this situation is being resolved, due to experiments being carried out
by Bohme and co-workers \(^{(37)}\) on a number of \(S_N^2\) reactions in the gas phase. Bohme reports results which are consistent with those predicted by theory. \(^{(38,39)}\)

B) SCF Results

Roothaan Hartree-Fock SCF\(^{(40)}\) calculations have recently been performed\(^{(41)}\) in this laboratory for a number of points along the minimum potential energy surface for two nucleophilic displacement reactions. The systems studied were the attack of the nucleophiles \(F^-\) and \(CN^-\) on the substrate \(CH_3F\). \(F^-\) is the leaving group in each case.

\[
F^- + CH_3F \rightarrow [F-CH_3-F]^- + CH_3F + F^- \tag{3.1}
\]
\[
CN^- + CH_3F \rightarrow [NC-CH_3-F]^- + CH_3CN + F^- \tag{3.2}
\]

The entity in the square brackets represents the transition state of the reaction.

The wavefunctions for all species present in reactions (3.1) and (3.2) are single determinantal and close to the Hartree-Fock limit. The absolute energies obtained in a Hartree-Fock calculation are in some error but for most problems of chemical interest one is concerned with energy differences so that errors in the absolute energies are not important.* However, one must still be

*There are two major factors leading to errors in the Hartree-Fock approximation of the total energy: relativistic effects and electron correlation. Estimates of the relativistic correction for atoms\(^{(42)}\) indicate that contributions from the valence shell are negligible (at least for first-row atoms) and that the relativistic energy of core electrons remains almost unchanged during the course of a chemical reaction. The correlation energy is defined as\(^{(43)}\) the difference between the Hartree-Fock energy and the exact nonrelativistic energy. This so-called correlation error reflects the fact that coulombic interactions between pairs of electrons, especially those with antiparallel spins, are not properly accounted for.
careful. In general, a single determinantal wavefunction, whether or not it is at the Hartree-Fock limit, does not provide an adequate description of a reaction process over the complete range of internuclear separations, because of the failure of such a wavefunction to properly describe the possible dissociation products of the reaction. This situation arises in those cases where dissociation leads to a decrease in the number of electron pairs. (For example, reactions of the type $A-A \rightarrow 2A$ where a single electron pair bond has been broken.) Reactions in which the dissociation products correspond to closed-shell systems are properly described within the Hartree-Fock approximation by single determinantal wavefunctions. Also, major changes in the correlation energy will occur only when the number of electron pairs is not conserved during the course of the reaction. Therefore, reactions involving closed-shell reactants and products, such as the ones being studied in the present work, should be accompanied by only small changes in the correlation energy, and consequently, the Hartree-Fock treatment should provide reasonable estimates of the heats of reaction for such systems. ($^{44,45,46}$)

Careful geometry optimizations were performed for most points on the surfaces. Because of the large number of basis functions required to yield a reliable description of $\text{FCH}_3\text{CN}^-$, only the F-C and C-CN bond lengths were optimized. The C-N bond length was taken to be that found in the $\text{CN}^-$ ion, the CH bond length was assumed to be the same as in $\text{FCH}_3\text{F}^-$, and the methyl group was taken as planar. For the details regarding the computations, the choice of basis sets, and the geometry optimizations, see reference
(41).

The geometry of the transition state of reaction (3.1) was calculated to be symmetric (having $D_{3h}$ symmetry) and to have energy 7.26 kcal/mole higher than the reactants. This is in good agreement with the value of 7.9 kcal/mole reported by Dedieu and Veillard$^{(38)}$ in their study of this and three other $S_N2$ type displacements using a slightly smaller basis set. Aside from the protons, the transition state in reaction (3.2) was assumed to be linear ($C_{3v}$ symmetry) and lead to an activation energy of 22.6 kcal/mole. The overall reaction was computed to be endothermic by 5.24 kcal/mole. For both reactions, the existence of an appreciable activation energy ($E_A > 5$ kcal/mole) is supported by the work of Bohme et al.$^{(37)}$

The $\text{FCH}_3\text{CN}^-$ transition state has a very extended C-F bond length of 4.225 au compared with 3.586 au in $[\text{FCH}_3\text{F}]^-$ and 2.650 au in CH$_3$F. This very unsymmetrical geometry of $[\text{FCH}_3\text{CN}]^-$ is in accord with the Hammond-Polanyi postulate$^{(47,48)}$ which states that the transition should closely resemble the products in a highly endothermic reaction.

(C) **Partitioning Results**

Closed shell HF-SCF calculations, by virtue of their close agreement with experimental results,$^{(49)}$ provide a reliable account of the total energy changes along a reaction path. Through the application of the Virial Partitioning Theory it becomes possible to localize into regions of real space the energy changes and interactions which underlie the gross thermochemistry. With this
in mind, a detailed look at the activation energies for the two reactions quoted is pursued.

The energetics of displacement reactions have in the past been analyzed from the view of bond formation versus bond breaking. The treatment in terms of virial fragments is a much more powerful approach because (1) vague notions associated with the concept of a bond are eliminated, and (2) the changes in the total energy of the system can be related to the energy changes that take place within the quantum subspaces defined by the virial fragments.

All products and reactants are initially at their ground state equilibrium geometries. Also, the transition state species of FCH$_3$F$^-$ and FCH$_3$CN$^-$ represent metastable, zero force structures. Thus the stability of any fragment at these particular points on the reaction surface is monitored by its kinetic energy. This quantity along with the other energy components comprising the total virial are recorded in Table 3.1. Of greater interest are those changes incurred by each fragment on passage to the transition state. These results are summarized in Table 3.2.

The initial stage of the S$_N$2 reaction corresponds to the attack of the nucleophile and subsequent formation of the transition state. During this process the nucleophilic species of both reactions increase in stability from that of its corresponding negative ion. At the transition state this increased stability amounts to 60 and 22 kcal/mole for the nucleophilic (F) and (CN) fragments respectively. These energies constitute negative contributions to the activation energies of the corresponding reactions.
<table>
<thead>
<tr>
<th>Molecule or Ion</th>
<th>Fragment (( \Omega ))</th>
<th>( \overline{N}(\Omega) ) (au)</th>
<th>( \overline{T}(\Omega) = -\overline{E}(\Omega) ) (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{F} )</td>
<td>( \text{CH}_3 )</td>
<td>8.2835</td>
<td>39.2467</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5.2973</td>
<td>37.3466</td>
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<tr>
<td></td>
<td>H</td>
<td>0.9954</td>
<td>0.6334</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>9.7165</td>
<td>99.7730</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} )</td>
<td>( \text{CH}_3 )</td>
<td>8.6603</td>
<td>39.4647</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5.7874</td>
<td>37.6556</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.9577</td>
<td>0.6030</td>
</tr>
<tr>
<td></td>
<td>CN</td>
<td>13.3397</td>
<td>92.3924</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>4.8960</td>
<td>37.1882</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8.4437</td>
<td>55.2042</td>
</tr>
<tr>
<td>( \text{FCH}_3\text{F}^- )</td>
<td>( \text{CH}_3 )</td>
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<td>39.3535</td>
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<tr>
<td></td>
<td>C</td>
<td>5.5373</td>
<td>37.5302</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.9115</td>
<td>0.6078</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>9.8641</td>
<td>99.5457</td>
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<tr>
<td>( \text{FCH}_3\text{CN}^- )</td>
<td>( \text{CH}_3 )</td>
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</tr>
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<td></td>
<td>H</td>
<td>0.9218</td>
<td>0.6081</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>9.9544</td>
<td>99.5074</td>
</tr>
<tr>
<td></td>
<td>CN</td>
<td>13.5966</td>
<td>92.2739</td>
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<tr>
<td></td>
<td>C</td>
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<td>N</td>
<td>8.5745</td>
<td>55.1570</td>
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<td>( \text{F}^- )</td>
<td>F</td>
<td>10.0000</td>
<td>99.4522</td>
</tr>
<tr>
<td>( \text{CN}^- )</td>
<td>( \text{CN}^- )</td>
<td>14.0000</td>
<td>92.2458</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>N</td>
<td>8.7784</td>
<td>55.2786</td>
</tr>
</tbody>
</table>
Table 3.2

Kinetic and Potential Energies of Activation and Population Changes for Fragments

<table>
<thead>
<tr>
<th></th>
<th>ΔC(Ω) (a)</th>
<th>ΔT(Ω) = -ΔE(Ω) kcal/mole</th>
<th>ΔV′(Ω) (b) au</th>
<th>ΔV''(Ω) au</th>
<th>ΔV''(Ω) au</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C) (-0.240)</td>
<td>+117</td>
<td>-12.013</td>
<td>6.315</td>
<td>5.326</td>
<td></td>
</tr>
<tr>
<td>(H) (+0.084)</td>
<td>-15</td>
<td>-1.320</td>
<td>0.777</td>
<td>0.591</td>
<td></td>
</tr>
<tr>
<td>(CH₃) (+0.012)</td>
<td>+72</td>
<td>-15.974</td>
<td>8.646</td>
<td>7.101</td>
<td></td>
</tr>
<tr>
<td>(F) (-0.147)</td>
<td>-139</td>
<td>-6.114</td>
<td>4.814</td>
<td>1.743</td>
<td></td>
</tr>
<tr>
<td>(F⁻) (+0.136)</td>
<td>+60</td>
<td>-35.835</td>
<td>17.253</td>
<td>18.390</td>
<td></td>
</tr>
</tbody>
</table>

CH₃F + CN⁻

<table>
<thead>
<tr>
<th></th>
<th>ΔC(Ω)</th>
<th>ΔT(Ω) = -ΔE(Ω) kcal/mole</th>
<th>ΔV′(Ω) au</th>
<th>ΔV''(Ω) au</th>
<th>ΔV''(Ω) au</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C) (-0.387)</td>
<td>+164</td>
<td>-14.813</td>
<td>7.604</td>
<td>6.687</td>
<td></td>
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<tr>
<td>(H) (+0.073)</td>
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<td>-1.690</td>
<td>0.945</td>
<td>0.792</td>
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<td>-19.883</td>
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<tr>
<td>(F) (-0.237)</td>
<td>-163</td>
<td>-5.900</td>
<td>5.034</td>
<td>1.384</td>
<td></td>
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<tr>
<td>(CN⁻) (+0.403)</td>
<td>+22</td>
<td>-41.011</td>
<td>19.575</td>
<td>21.366</td>
<td></td>
</tr>
<tr>
<td>(C) (+0.200)</td>
<td>+97</td>
<td>-20.208</td>
<td>9.592</td>
<td>10.308</td>
<td></td>
</tr>
<tr>
<td>(N) (+0.203)</td>
<td>-75</td>
<td>-20.803</td>
<td>9.983</td>
<td>11.058</td>
<td></td>
</tr>
</tbody>
</table>

(a) ΔC(Ω) = C(Ω, transition state) - C(Ω, reactant). A negative ΔC(Ω) implies an increase in the electron population.

(b) 1 au of energy = 627.71 kcal/mole.
Occurring simultaneously with the attack of the nucleophiles is the departure of the leaving group - the fluorine fragment. In contrast to the nucleophilic fragments, the departing (F) fragment becomes considerably destabilized during the reaction process. Relative to its value in CH₃F, the reactant molecule, the energy of the (F) fragment increases (i.e., is destabilized) by the amount of 139 kcal/mole from its value in the [FCH₃F⁻]⁻ transition state of reaction (3.1). Similarly, for reaction (3.2), the (F) fragment is 163 kcal/mole less stable in the [FCH₃CN⁻]⁻ transition state than in the reactant molecule, methyl fluoride. As these energy changes act to destabilize the system at the transition state, they contribute positively to the activation energy for each reaction.

One must also consider the energy changes of the (CH₃) fragment arising from the interactions with both nucleophile and leaving group. The transition state energies of the methyl fragment are 72 and 119 kcal/mole lower than their energies in CH₃F for reactions (3.1) and (3.2) respectively. Thus (CH₃) is also stabilized at the transition state.

These results show that the only factor contributing to the increased energy of the transition state in both reactions is the destabilization of the leaving (F) fragment; all other fragments (CH₃ being considered as one fragment) act to lower the total energy along the reaction path.

It is of interest to note that in the [FCH₃CN⁻]⁻ transition state the energy of the (F) fragment is only 36 kcal/mole more stable than that of the free fluoride ion (Table 3.1). In terms
of the bond making/breaking approach this fact is indicative of
the extent to which bond breaking has progressed at the transition
state.

Because of the virial relationship the stability of a frag-
ment is open to further examination in terms of the various inter-
actions which ultimately determine its total energy. Referring
to Table 3.2, it is seen that the primary source of stability of
the incoming nucleophile is from increased electron-nuclear inter-
actions. This is to be expected. The attractive potential of the
nucleophilic charge density with the nuclei of the substrate,
$\nabla'_{\text{CH}_3\text{F}}$ (nucleophile), will increase sharply with decreasing distance
between them. The specific breakdown is given in Table 3.3. The
magnitude of $\Delta \nabla'_{\text{CH}_3\text{F}}$ (nucleophile) is greater than the magnitude of
$\Delta \nabla'_{\text{F}}$ (nucleophile) because of the closer proximity of the nuclei
in ($\text{CH}_3$) to the charge density of the nucleophile. The small
decrease in $\Delta \nabla'_{\text{\Omega}}$ (\Omega) where (\Omega) represents the nucleophilic fragment,
is attributed to the diminished population of this fragment.

Also listed in Table 3.3 is the corresponding breakdown of
$\Delta \nabla'$ for the leaving (F) fragment. Here there are two main and
opposing considerations. The interaction of (F) with the nucleo-
phile increases with decreasing separation between them. Similarly,
as bond breaking progresses, the charge density in (F) interacts
less with the nuclei of the methyl group. As seen in Table 3.3
for the $\text{CN}^- + \text{CH}_3\text{F}$ reaction, the stabilization gained by (F) from
the attraction of the charge density of the approaching ($\text{CN}^-$) is
15.1022 au at the transition state. Similarly the decreased inter-
actions with the charge density of the methyl group accounts for a
Table 3.3

Breakdown of $\Delta V'$ for the Attacking and Leaving Fragments\(^{(a)}\)

<table>
<thead>
<tr>
<th>Values are in au.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta V^\prime_\Omega(\Omega)$</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>$R_x(3.1)$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>$R_x(3.2)$</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) $\Delta V^\prime(\Omega) = V^\prime(\Omega, \text{transition state}) - V^\prime(\Omega, \text{reactant})$

\(^{(b)}\) $F^-$ and $\text{CN}^-$ represent the nucleophiles for the respective reactions.

decrease in stabilization of 9.3987 au for the departing (F) fragment. Thus, overall, the leaving group is stabilized with respect to changes in $V'$.

The data in Table 3.2 reveals that on the formation of the transition state every fragment experiences a destabilizing increase in both electron-electron repulsions and nuclear-nuclear repulsions. $V''(\Omega)$ may be subdivided in a manner analogous to that performed above on $V'(\Omega)$. The discussion subsequent to this breakdown would also closely parallel the one just given for $V'(\Omega)$ as the interactions are basically equivalent. In short, the large positive value for $\Delta V''(\text{nucleophile})$ is due to the added repulsions with the substrate electrons. As before, $\Delta V''$ for the leaving group is the resultant of two opposing factors. Its positive sign is testimony to the predominance of the repulsive
interactions with the nucleophile.

In general, for the approach of two separate, neutral, spherical (unpolarized) charge distributions, the sum of the changes in $\Delta V'$, $\Delta V''$ and $\Delta V_n$ will vanish. For this special case $\Delta V'' = \Delta V_n = -\frac{1}{2} \Delta V'$. Reference to Table 3.2 indicates that this particular relationship is followed quite closely by all fragments with the exception of the leaving group. It is the small departure from this delicate balance in the potential energies which determines whether the attractive or repulsive interactions dominate the energy changes for a given fragment and determine whether the fragment is stabilized or destabilized in the process.

In summary, the activation energy results solely from the destabilization of the leaving group. The larger activation energy for the $\text{CN}^- + \text{CH}_3\text{F}$ reaction is due to the greater extent to which the leaving (F) fragment has separated from the substrate at the $[\text{FCH}_3\text{CN}]^-$ transition state relative to that in $[\text{FCH}_3\text{F}]^-$. A discussion of the two reactions is not complete without an analysis of the charge distributions and changes therein. Contour maps of the electronic charge density with the partitioning surfaces added are shown in Figures 3.1 and 3.2. Also shown are the net charges, $\bar{Q}(n)$, associated with each fragment. These plots together with the population changes listed in Table 3.2 make quantitative a great deal of intuitive chemical ideas.

An isolated, closed-shell, mononuclear fragment is described by a spherical charge distribution governed by a single, central nuclear force. The extent to which the spherical nature of the charge density is retained is determined by the relative strengths
Figure 3.1

Contour maps\textsuperscript{a} of the electronic charge densities for the reactants, $F^-$ and $\text{CH}_3\text{F}$, and the transition state, $\text{FCH}_3\text{F}^-$, for the corresponding $S_{N2}$ reaction (in which $F^-$ and $\text{CH}_3\text{F}^-$ are also products). The virial partitioning surfaces and fragment net charges are also shown.

Plot A; $F^-$
Plot B; $\text{CH}_3\text{F}$
Plot C; $\text{FCH}_3\text{F}^-$

\textsuperscript{a}For contour values see caption for Figure 2.1.
Figure 3.2

Contour maps\(^a\) of the electronic charge densities for \(\text{CN}^-\), \(\text{FCH}_3\text{CN}^-\), the transition state in the \(S_{\text{N}2}\) reaction of \(\text{CN}^-\) with \(\text{CH}_3\text{F}\), and \(\text{CH}_3\text{CN}\), a product in the \(S_{\text{N}2}\) reaction. The virial partitioning surfaces and fragment net charges are also shown. The maps correspond as follows:

Plot A; \(\text{CN}^-\)
Plot B; \(\text{FCH}_3\text{CN}^-\)
Plot C; \(\text{CH}_3\text{CN}\)

\(^a\)For contour values see caption for Figure 2.1.
Figure 3.3

Contour maps\textsuperscript{a} of electronic charge densities showing changes incurred in the F\textsuperscript{−} fragment upon C-F bond formation. From top to bottom the plots correspond to:

\begin{tabular}{ll}
  F\textsuperscript{−} & R\textsubscript{F-C} = \infty \\
  (F) in FCH\textsubscript{3}CN\textsuperscript{−} & R\textsubscript{F-C} = 4.255 \text{ au} \\
  (F) in FCH\textsubscript{3}F\textsuperscript{−} (D\textsubscript{3}h) & R\textsubscript{F-C} = 3.586 \text{ au} \\
  (F) in FCH\textsubscript{3} & R\textsubscript{F-C} = 2.650 \text{ au} \\
\end{tabular}

\textsuperscript{a}For contour values see caption for Figure 2.1.

\textsuperscript{b}R\textsubscript{F-C} represents the fluorine-carbon bond length.
of the internal and external forces exerted on the fragment. The resistance to distortion is closely associated with the concepts of electronegativity and polarizability. The fluorine fragment is characterized by a large net negative charge and a strong central force field. The pronounced "pinched" effect of the density contours at the fragment boundary are indicative of the strong central field.

An interesting contrast in nucleophilic behaviour is provided by the F⁻ and CN⁻ ions in these reactions. Whereas F⁻ is a hard spherical ion, the charge density in CN⁻ is highly polarized with the nitrogen end carrying a net negative charge of over 1.7 e⁻. Nucleophilic attack by CN⁻ apparently takes place via the electrophilic end of the ion. Charge is transferred to the substrate with the approach of CN⁻ but the extreme polarization of charge is still maintained at the transition state. Both the (C) and the (N) fragments contribute nearly equal amounts of 0.20 e⁻. By comparison, the F⁻ ion transfers only 0.136 e⁻ or approximately one-third that of CN⁻.

Much of the charge transfer from the nucleophile is taken up by the leaving group. In fact, for the F⁻ + CH₃F reaction, the charge gained by the departing (F) fragment slightly exceeds the amount received from F⁻. In the transition state of FCH₃CN⁻ the population of the F⁻ fragment is 9.954 e⁻, an increase of 0.237 e⁻ from its value in CH₃F and only 0.046 e⁻ less than that of an isolated F⁻ ion. The incipient formation of F⁻ at this point in the reaction is evident from the contour plots of Figure 3.3. As the F-C internuclear distance is increased in the series CH₃F,
FCH$_3$F$^-$, NCCH$_3$F$^-$, the identity of the F fragment more closely approaches the limiting case of F$^-$ (as determined by the number of closed contours which encompass only the fluorine nucleus).

The population of the methyl fragment remains nearly constant throughout the F$^-$ + CH$_3$F reaction. In the transition state where (CH$_3$) is positioned between two electronegative F fragments, $N$(CH$_3$) decreases by only 0.012 electrons from its value of 8.28 e$^-$ in CH$_3$F. In the CN$^-$ + CH$_3$F reaction charge is transferred into the methyl fragment from the approaching CN fragment so that the population of (CH$_3$) at the FCH$_3$CN$^-$ transition state is 0.168 e$^-$ larger than that in CH$_3$F. As the reaction proceeds to products, a further 0.211 e$^-$ is transferred to (CH$_3$) which attains a population 8.66 e$^-$ in CH$_3$CN.

A breakdown of the population within the methyl fragment reveals that in the reactant molecule, CH$_3$F, the H fragment is essentially neutral ($\overline{C}$(H) = 0.005). Thus, the net charge of 0.72 for (CH$_3$) is almost entirely localized within the carbon fragment. Nucleophilic attack by either F$^-$ or CN$^-$ on CH$_3$F induces a charge flow within the methyl group from (H) to (C). In the transition state species of FCH$_3$F$^-$ and FCH$_3$CN$^-$ the net charges on the H fragments are increased to 0.089 and 0.078 respectively. As the reaction proceeds past the transition state the direction of charge flow reverses with the result that $\overline{C}$(H) is reduced to 0.005 and 0.042 e$^-$ in the respective product molecules of CH$_3$F and CH$_3$CN for reactions (3.1) and (3.2).

It is reasonable to ask the question of why, in CH$_3$F, there has not been more charge transferred from (H) to (C) so that the
net charge of the carbon fragment would be delocalized to a greater extent over the methyl fragment. The fluorine fragment which adjoins the carbon fragment in CH$_3$F is characterized by a tight distribution of charge density and a large net negative charge of $\approx 0.72$ e$^-$. Consequently, the F fragment is the source of a relatively strong negative or repulsive field which is exerted on the charge density in the neighbouring C fragment. Thus any charge transferred from (H) to (C) in this molecule would increase the total energy of the system by contributing to large increases in electron-electron repulsions in the carbon fragment.

In methyl cyanide, a repulsive field similar to the one emanating from (F) in CH$_3$F is not present. The carbon fragment of the cyano group has a net positive charge and a charge density which is considerably more polarizable than that of the F fragment. In CH$_3$CN, therefore, there is a significant transfer of charge from (H) to (C) in spite of the fact the net positive charge on (CH$_3$) is reduced relative to its value in CH$_3$F.*

The fragment populations within the methyl group in the transition state species appear to be at variance with the above generalizations. This is particularly so for $\text{FCH}_3^-$ where (C) is

*Results similar to those quoted for CH$_3$F and CH$_3$CN are also found in the corresponding systems of BH$_3$F$^-$ and BH$_3$CO$_2$. The population of (H) in BH$_3$F$^-$ increases relative to the population of (H) in BH$_3$, but decreases in the formation of BH$_3$CO. Like the C fragment in (CN) the C fragment in (CO) has a relatively large net positive charge.
bonded linearly to two negatively charged F fragments. In this species the hydrogen as well as the carbon fragment comes under the direct influence of the repulsive field generated by the F fragment. Each H fragment is destabilized by \( \sim 15 \text{ kcal/mole} \) in the transition state relative to \( \text{CH}_3\text{F} \), a result of the increase in the electron-electron and nuclear repulsion forces exceeding the increase in electron-nuclear attractive interactions. In order to minimize the total energy of the system, charge is transferred from (H) to (C); a region where attractive interactions are maximized.

The anomalous behaviour discussed above may also be argued in terms of a "crowding" of the H fragments in the transition state. From Figures 3.1 and 3.2 it is clear that the presence of the (F) in the species \( \text{FCH}_3\text{F}^- \) and \( \text{FCH}_3\text{CN}^- \) reduces the effective volume of space occupied by the H fragments. An integration of the hydrogen fragment volumes out to the outermost contour (the 0.002 au contour) illustrated in the figures indicates that the volume occupied by the charge distribution of the H fragment in \( \text{CH}_3\text{F} \) is decreased by 12% in the formation of \( \text{FCH}_3\text{F}^- \). The same decrease in the spatial extent of the H fragment is evident in the \( \text{FCH}_3\text{CN}^- \) transition state. The nonbonded radius of (H) (the distance from the proton to the 0.002 au contour on the nonbonded side of the C-H internuclear axis) remains at a value of \( \sim 2.2 \text{ au} \) in \( \text{CH}_3\text{F} \) and both transition states. Thus, it is energetically more favourable for a compressed H fragment to transfer charge out and into a neighbouring fragment rather than transfer it to its nonbonded region. Note that the changes in energy of (H) on formation of the transition state
May be rationalized in terms of the quantum mechanical uncertainty relation whereby the total energy of the system must increase if the volume is decreased.

The 45 \((= 3 \times 15)\) kcal/mole "compression energy" stored in the hydrogen fragments is released as the system goes to products. The release of this energy, coupled with further bond formation with the nucleophile, serves as a driving force for further motion along the reaction coordinate. Thus, one may via the virial partitioning theory isolate those spatial regions or fragments in a reacting system in which potential energy is accumulated and later released, either to drive the same reaction to completion or to initiate a subsequent one. This ability to identify spatially the "energy rich" regions of a molecular system can be used to quantify the concept of "high energy bonds" and the role they are assigned in biochemical reactions.
CHAPTER 4

THE GEOMETRY OF SIMPLE HYDRIIDE MOLECULES

(A) Introduction

The understanding and explanation of the geometry of molecules has posed a perplexing problem for scientists throughout the development of modern chemistry. In spite of the vast amount of effort channelled into this subject a fundamental understanding of molecular geometry still does not exist. While there are several models\(_{51,52,53,54}\) which correctly account for the shapes of large numbers of molecules, none of these models provide a basic understanding of underlying principles, since they fail to relate to the total energy of the system— the ultimate factor determining the shape of a molecule. Presented in this chapter are observations of how the energy and the charge distribution change as the molecular geometry is varied. Through the use of virial partitioning theory changes in the total energy and its potential energy components as well as changes in the charge distribution are investigated in terms of their spatially localized contributions. From a knowledge of these localized changes one is able to relate the change in the total energy which accompanies a change in molecular geometry to the changes which occur in the molecular charge distribution. That is, no modelling is performed. Instead, one observes what the changes in the energy and the charge
distribution are, and through the use of the virial partitioning procedure, one is able to rationalize one in terms of the other.

The ground state energies as a function of molecular geometry are investigated for the following series of \( \text{AH}_n \) molecules: \( \text{BeH}_2, \text{BH}_3, \text{NH}_3 \), and \( \text{H}_2\text{O} \). The main thrust of the present work is toward a better understanding of the contrasting structural differences exhibited by these four molecules and, specifically, toward an understanding of factors underlying the differentiation of linear and non-linear \( (C_{2v}) \) structures and of planar and non-planar \( (C_{3v}) \) structures. Accordingly, each molecule is studied in its two contrasting geometric forms, that is, both a linear and a non-linear geometry and \( \text{H}_2\text{O} \) and \( \text{BeH}_2 \) as well as a planar and non-planar geometry of \( \text{NH}_3 \) and \( \text{BH}_3 \) are considered. The specific geometries chosen are those corresponding to special points (minima or maxima) on the molecular potential surface. Included are the respective stable equilibrium bent and pyramidal geometries of \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) (geometries at a potential minimum) as well as their respective pseudo-equilibrium linear and planar geometries (geometries at a potential maximum). Each of these geometries, by virtue of their being at minimum or maximum points on the potential surface, are zero-force geometries; that is, geometries for which there are no net forces acting on the nuclei. For linear \( \text{H}_2\text{O} \) and planar \( \text{NH}_3 \), the criterion of zero net forces guarantees that one has the lowest point on the potential
surface for these forms of the molecules. The molecules BeH$_2$ and BH$_3$ each possess one zero-force structure—this being their respective linear and planar stable equilibrium structures. All non-linear or non-planar forms of these two molecules are characterized by the presence of net forces which act to return the molecules to their equilibrium geometries. In view of this, the respective $C_{2v}$ and $C_{3v}$ geometries for BeH$_2$ and BH$_3$ were obtained as follows: The H–A–H (A = Be or B) angles were set to the tetrahedral angle of 109.5° and the A–H bond lengths were then optimized to eliminate the stretching component of the net force acting on the protons. Therefore, the bond lengths in these geometries are at their equilibrium values with respect to bond stretching.

(B) Wavefunctions and SCF Results

For the H$_2$O molecule the (10, 6, 2/4, 2) uncontracted gaussian basis set of Neumann and Moskowitz (55) was employed. A total energy of -76.05936 au was obtained by these authors for the geometry $R_{OH} = 1.80$ au and $\text{HOH} = 105.0^\circ$. (Their total energy is estimated (55) to be within 0.03 au of the Hartree-Fock limit for H$_2$O). In the present study the geometry was optimized to eliminate net forces on the protons. Such an optimization resulted in a lowering of the total energy to -76.05964 au at the geometry $R_{OH} = 1.79682$ and $\text{HOH} = 106.142^\circ$. Experimental values for the equilibrium

*This geometry differs slightly from that yielding a minimum in the total energy (an energy minimum of -76.05967 was
geometry of H₂O are: \( R_{OH} = 1.8087 \text{ au} \) and \( \text{HOH} = 107.52^\circ \).

The energy difference between the two zero-force structures of H₂O was computed to be 0.053 au (33.3 kcal/mole).

The wavefunctions for both the planar and pyramidal forms of NH₃ are those reported by Rauk, Allen and Clementi in their study of the barrier to inversion in this molecule. These workers contracted a (13, 8, 2/8, 2) gaussian basis set to a \([8, 5, 2/4, 1] \) set, and, with d-exponent optimization, obtained an energy minimum of -56.2219 au - a value estimated to be 0.002 to 0.003 au above the Hartree-Fock limit. This energy minimum corresponds to the geometry (experimental values are in brackets): \( R_{NH} = 1.8903 \text{ au} \) (1.9117 au) and \( \text{HNH} = 107.2^\circ \) (106.7°). Their reported value of 5.08 kcal/mole for the inversion energy of NH₃ compares well with the experiment value of 5.8 kcal/mole. (The NH₃ calculations cited above were repeated by the author and complete agreement of results was obtained. The geometries quoted are very close to being zero-force geometries, i.e. the net forces on the protons are less than 0.015 au.)

Wavefunctions for the two forms of BeH₂ were generated by the author using a (10, 6, 1/4, 2) basis set comparable to that

*obtained at the geometry \( R_{OH} = 1.79467 \) and \( \text{HOH} = 106.0^\circ \). The slight difference is due to the fact that LCAO-MO SCF wavefunctions, even those with extended basis sets, do not, in general, satisfy exactly the Hellmann-Feynman and virial theorems. This small inaccuracy in the wavefunction gives rise to small fictitious net forces which persist in all geometries near and including the lowest energy geometry. The zero-force geometries referred to in this study imply zero net forces on the protons.
used for the H₂O molecule. The Be (10, 6) set of Kaufman et al. was augmented with a complete set of d functions (exponent = 0.6) while the (4, 2) set of Neumann and Moskowitz was centered on the H's. The zero-force geometry of BeH₂ was calculated to be \( R_{\text{BeH}} = 2.5582 \) au and \( \angle \text{BeH} = 180^\circ \); a geometry which also corresponds to the energy minimum of -15.7708 au for this molecule. Although an experimental geometry for BeH₂ has not as yet been reported the results given here are in accord with earlier theoretical studies.

Wavefunctions for the BH₅ structures were those obtained by G. Runtz of this laboratory. The basis set includes a [5, 3] contraction of Huzinaga's Boron (10, 6), together with a 4s contraction of Huzinaga's 6s set for the hydrogens. The set was then extended with a complete set of d functions (exponent = 0.57) centered on the boron and a complete set of p functions (exponent = 1.00) centered on each hydrogen. This extended basis set yielded a total energy of -26.4000 au for BH₅ at its planar equilibrium geometry (\( R_{\text{B-H}} = 2.2500 \) au).

A complete summary of structural and SCF data for the four molecules in each of their two conformations is collected in Table 4.1. With regard to the structural data, it is noted that the A-H bond lengths in all four molecules are longer in the C₂ᵥ or pyramidal structures than in the corresponding.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym.</th>
<th>HAH (au)</th>
<th>RAH, H (au)</th>
<th>$\bar{E}_T$ (au)</th>
<th>$\bar{V}_\text{eff}$ (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeH$^+$</td>
<td>C$_2v$</td>
<td>109.5</td>
<td>15.7112</td>
<td>-42.7454</td>
<td>7.1283</td>
</tr>
<tr>
<td></td>
<td>D$_{oh}$</td>
<td>120.0</td>
<td>15.7708</td>
<td>-42.7954</td>
<td>7.4456</td>
</tr>
<tr>
<td>BH$_3$</td>
<td>C$_3v$</td>
<td>109.5</td>
<td>15.7112</td>
<td>-42.7454</td>
<td>7.1283</td>
</tr>
<tr>
<td></td>
<td>D$_{3h}$</td>
<td>120.0</td>
<td>15.7708</td>
<td>-42.7954</td>
<td>7.4456</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>C$_3v$</td>
<td>109.5</td>
<td>15.7112</td>
<td>-42.7454</td>
<td>7.1283</td>
</tr>
<tr>
<td></td>
<td>D$_{3h}$</td>
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<td>15.7708</td>
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<td>7.4456</td>
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<tr>
<td>H$_2$O$^-$</td>
<td>C$_2v$</td>
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<td>120.0</td>
<td>15.7708</td>
<td>-42.7954</td>
<td>7.4456</td>
</tr>
</tbody>
</table>
linear or planar structures.* This is especially significant in view of the fact that all bond lengths in these structures are at equilibrium values with respect to bond stretching. Changes in interatomic distances directly affect molecular energetics through changes in the nuclear-nuclear repulsions, \( V_n \). The longer bond lengths in the bent forms of these molecules reduces \( V_n \) from the value it would have if \( R_{A-H} \) remained unchanged. In fact, the nuclear-nuclear repulsions in the bent forms of \( H_2O \), \( NH_3 \) and \( BeH_3 \) are less than those in the corresponding linear or planar forms of the molecules.

Energy changes between two geometric forms of a molecule can be related by the equation

\[
\Delta E = \Delta T + \Delta V' + \Delta V'' + \Delta V_n
\]

(4.1)

For any change resulting in a more stable structure the change in the total energy will be negative, i.e., \( \Delta E < 0 \).**

* The observed direction of change of A-H bond lengths is not confined to the molecules of Table 4.1. Similar results have been found for the PH\(_3\) molecule (66) as well as for transition state species of the type \( X^-CH_3-Y^+ \) occurring in the \( S_n^2 \) reactions discussed in the previous chapter.

** If the wavefunctions satisfy the virial theorem exactly then the total energy change is also given by the virial relation

\[
\Delta E_{\text{virial}} = \frac{1}{2}(\Delta V' + \Delta V'' + \Delta V_n)
\]

(4.1a)

Due to the inaccuracies of the wavefunctions employed (see footnote on pg. 82) \( \Delta E \) calculated from equation (4.1a) is not in total agreement with the actual total energy change (\( \Delta E_{\text{actual}} \)) calculated from equation (4.1). However, the difference in the two values of \( \Delta E \) is always much less than any of the individual potential energy changes. The magnitude of the difference between the values obtained for \( \Delta E \) using eq. (4.1) and eq. (4.1a) is to be compared with the magnitudes of the individual contributions to \( \Delta V \) as the error is spread over each of the potential energy contributions to \( \Delta E \). For the molecules listed in Table 4.2, the values of \( \Delta E_{\text{actual}} - \Delta E_{\text{virial}} \) are as follows: \( \text{BeH}_2, 0.0005 \text{ au}; \text{BH}_3, 0.0781 \text{ au}; \text{NH}_3, 0.0044 \text{ au}; \text{H}_2O, 0.0009 \text{ au}. \)
In general, a molecular system may be stabilized either by increases in $|\bar{V}'|$ , the magnitude of the average electron-nuclear attractive interactions, or by decreases in $\bar{V}''$ or $V_n$, the average electron-electron and nuclear-nuclear repulsive interactions, respectively. For the special case of bond formation from isolated atoms, the accompanying increase in stabilization is achieved through an increase in electron-nuclear attractions; an increase which is larger than the simultaneous and destabilizing increases in the repulsive interactions. Thus, molecular stability arising from bond formation is characterized by negative $\Delta \bar{E}$ and $\Delta \bar{V}'$ values together with positive values for $\Delta \bar{V}''$ and $\Delta \bar{V}_n$ such that $|\Delta \bar{V}'| > \Delta \bar{V}'' + \Delta \bar{V}_n$ and hence $\Delta \bar{E} < 0$.

Table 4.2 shows the changes in energy between the two geometric conformation of each molecule. (The energy changes denoted in this table refer to the structural change leading to the most stable geometry. This convention, of considering the stabilizing structural change will, unless otherwise stated, be maintained throughout this chapter.) It is clear from the different patterns of energy changes recorded in Table 4.2 that the causes of geometric stability are neither similar to nor lend themselves to as straightforward an interpretation as those associated with bond formation. For $H_2O$ and $NH_3$, the increased stability of the bent and pyramidal
Table 4.2

SCF Energy Changes Between Geometric Conformations

<table>
<thead>
<tr>
<th>Mol., Structural Change&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\Delta E$ (au)</th>
<th>$\Delta T$ (au)</th>
<th>$\Delta V'$ (au)</th>
<th>$\Delta V''$ (au)</th>
<th>$\Delta V''$ (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BeH}<em>2: C_2v \rightarrow D</em>{\infty h}$</td>
<td>-0.0454</td>
<td>0.0443</td>
<td>-0.0500</td>
<td>-0.0362</td>
<td>-0.0035</td>
</tr>
<tr>
<td>$\text{BH}<em>3: C</em>{3v} \rightarrow D_{3h}$</td>
<td>-0.0434</td>
<td>0.1996</td>
<td>-0.8284</td>
<td>+0.2773</td>
<td>+0.3082</td>
</tr>
<tr>
<td>$\text{NH}<em>3: D</em>{3h} \rightarrow C_{3v}$</td>
<td>-0.0081</td>
<td>0.0168</td>
<td>+0.2319</td>
<td>-0.1304</td>
<td>-0.1265</td>
</tr>
<tr>
<td>$\text{H}<em>2\text{O}: D</em>{\infty h} \rightarrow C_{2v}$</td>
<td>-0.0530</td>
<td>0.0546</td>
<td>+0.2607</td>
<td>-0.2561</td>
<td>-0.1123</td>
</tr>
</tbody>
</table>

<sup>a</sup> See Table 4.1 for specific structural data.
structures, respectively, over the corresponding linear and planar geometries, result from decreases in the repulsive interaction energies, \( \overline{V}' \) and \( \overline{V}_{n} \). The average value of \( |\overline{V}'| \), the electron-nuclear attraction energy, is reduced in the equilibrium structures of both these molecules. In contrast to \( \text{H}_2\text{O} \) and \( \text{NH}_3 \), the energetically favoured planar structure of \( \text{BH}_3 \) owes its stability to an increase in the value of \( |\overline{V}'| \); the changes in the average repulsion energies are destabilizing. In the \( \text{BeH}_2 \) molecule, each of the potential energy functions, \( \overline{V}' \), \( \overline{V}'' \) and \( \overline{V}_{n} \), change in a direction which stabilizes the linear geometry of this molecule. Of these energy changes, \( \Delta \overline{V}' \) provides the largest stabilizing influence.

\( \text{H}_2\text{O} \) and \( \text{NH}_3 \) represent a class of molecules having non-bonded valence electron pairs while \( \text{BeH}_2 \) and \( \text{BH}_3 \) are representative of molecules whose entire valence shell electrons are involved in bonding. It is seen from Table 4.2 that these two groups of molecules behave differently when subjected to changes in geometry. For both \( \text{H}_2\text{O} \) and \( \text{NH}_3 \), decreases in the repulsive interactions are responsible for their stable geometries. The stable geometries of both \( \text{BeH}_2 \) and \( \text{BH}_3 \) are primarily a result of increases in the electron-nuclear attractions.

(C) Partitioning Results: Fragment Charge Distributions

The understanding of molecular geometry may be pursued
from two fronts. The first, to be discussed here, involves the analysis of the physical properties of the charge distribution and the changes in $\sigma(r)$ caused by variations in the nuclear framework. The second approach, to be discussed in the following section, considers changes in the energetics of the system. These two approaches are not unrelated but, as shown by the theorem of Hohnberg and Kohn, (21) must be complementary.

Contour maps of the ground state charge distributions for the bent and linear forms of both $\text{H}_2\text{O}$ and $\text{BeH}_2$, as well as the pyramidal and planar forms of both $\text{NH}_3$ and $\text{BH}_3$, appear in Figure 4.1. The maps for $\text{BH}_3$ and $\text{NH}_3$ (maps C through F) show the charge density in a $\sigma_v$ symmetry plane of these molecules. To each of the density maps in Figure 4.1, the zero-flux partitioning surfaces have been added.

Major differences between the charge distributions of $\text{H}_2\text{O}$ and $\text{NH}_3$, on the one hand, and of $\text{BeH}_2$ and $\text{BH}_3$, on the other, are clearly displayed as differences in the shapes of their respective partitioning surfaces. In the former molecules, the curvature of the surface from the internuclear null point bends back to encompass the protons; an indication of the positive net change of the H fragments. (At the equilibrium geometries of $\text{H}_2\text{O}$ and $\text{NH}_3$, the H fragment net charges are 0.607 and 0.364, respectively.)

In sharp
Figure 4.1

Contour maps\(^a\) of the electronic charge densities together with the virial partitioning surfaces for linear and bent forms of both BeH\(_2\) and H\(_2\)O and planar and pyramidal forms of both BH\(_3\) and NH\(_3\). The maps correspond to the following geometries:

\[
\begin{align*}
\text{BeH}_2 & \quad R_{\text{Be-H}} = 2.5582^b & \quad \text{BeH}_2^c & \quad R_{\text{Be-H}} = 2.5275 \\
& \quad \text{HBeH} = 109.5^\circ & & \quad \text{HBeH} = 180.0^\circ \\
\text{BH}_3 & \quad R_{\text{B-H}} = 2.3360 & \quad \text{BH}_3^c & \quad R_{\text{B-H}} = 2.2500 \\
& \quad \text{HBH} = 109.5^\circ & & \quad \text{HBH} = 120.0^\circ \\
\text{NH}_3^c & \quad R_{\text{N-H}} = 1.8903 & \quad \text{NH}_3 & \quad R_{\text{N-H}} = 1.8600 \\
& \quad \text{HNH} = 107.2^\circ & & \quad \text{HNH} = 120.0^\circ \\
\text{H}_2\text{O}^c & \quad R_{\text{O-H}} = 1.7960 & \quad \text{H}_2\text{O} & \quad R_{\text{O-H}} = 1.7611 \\
& \quad \text{HOH} = 106.1^\circ & & \quad \text{HOH} = 180.0^\circ \\
\end{align*}
\]

\(^a\)For contour values see caption for Figure 2.1. \\
\(^b\)Distances are given in atomic units. \\
\(^c\)Corresponds to the lowest energy geometry.
Table 4.3

Physical properties\textsuperscript{a} of the charge distributions of the H\textsubscript{2} fragments in the AH\textsubscript{n} systems

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Distance from H to null point, \textsuperscript{\textdagger}</th>
<th>Perpendicular distance of null point from bond axis \textsuperscript{c}</th>
<th>Charge density at null point \textsuperscript{d}</th>
<th>( \hat{F}_{\text{H}}(H) \textsubscript{L} )</th>
<th>( \hat{F}_{\text{H}}(H) \textsubscript{H} )</th>
<th>( \hat{\mu}(H) \textsubscript{L} )</th>
<th>( \hat{\mu}(H) \textsubscript{H} )</th>
<th>( \hat{N}(H) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeH\textsubscript{2}</td>
<td>C\textsubscript{2v} \textsuperscript{b}</td>
<td>1.4808</td>
<td>0.1420 \textsuperscript{c}</td>
<td>0.0905</td>
<td>0.0521 \textsuperscript{d}</td>
<td>-0.2232 \textsuperscript{e}</td>
<td>-0.3940 \textsuperscript{f}</td>
<td>0.5403 \textsuperscript{g}</td>
</tr>
<tr>
<td></td>
<td>D\textsubscript{o\textsuperscript{h}}</td>
<td>1.4400</td>
<td>0.0000</td>
<td>0.0968</td>
<td>0.0000</td>
<td>-0.2356</td>
<td>0.0000</td>
<td>0.5965</td>
</tr>
<tr>
<td>BH\textsubscript{3}</td>
<td>C\textsubscript{3v} \textsuperscript{b}</td>
<td>1.3771</td>
<td>0.1085</td>
<td>0.1648</td>
<td>0.0447</td>
<td>-0.3169</td>
<td>0.0000</td>
<td>1.6545</td>
</tr>
<tr>
<td></td>
<td>D\textsubscript{3h}</td>
<td>1.2976</td>
<td>0.0000</td>
<td>0.1839</td>
<td>0.0000</td>
<td>-0.3455</td>
<td>0.0000</td>
<td>1.7123</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>C\textsubscript{3v} \textsuperscript{b}</td>
<td>0.4957</td>
<td>-0.0058</td>
<td>0.3541</td>
<td>-0.0111</td>
<td>-0.0706</td>
<td>0.0069</td>
<td>-0.0933</td>
</tr>
<tr>
<td></td>
<td>D\textsubscript{3h}</td>
<td>0.4672</td>
<td>0.0000</td>
<td>0.3642</td>
<td>0.0000</td>
<td>-0.0534</td>
<td>0.0000</td>
<td>-0.0445</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>C\textsubscript{2v} \textsuperscript{b}</td>
<td>0.3598</td>
<td>-0.0062</td>
<td>0.3839</td>
<td>-0.0084</td>
<td>0.0320</td>
<td>0.0048</td>
<td>-0.1540</td>
</tr>
<tr>
<td></td>
<td>D\textsubscript{o\textsuperscript{h}}</td>
<td>0.3100</td>
<td>0.0000</td>
<td>0.3592</td>
<td>0.0000</td>
<td>0.0526</td>
<td>0.0000</td>
<td>-0.1033</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All data is in atomic units.

\textsuperscript{b}For structural data, see Table 4.1.

\textsuperscript{c}A positive value indicates a displacement into the binding region of the molecule.

\textsuperscript{d}A positive value for \( \hat{F}_{\text{H}}(H) \textsubscript{L} \) implies a force on the proton which would increase the HAH angle.

\textsuperscript{e}A positive value for \( \hat{F}_{\text{H}}(H) \textsubscript{H} \) implies a force on the proton which would increase the AH interatomic distance.

\textsuperscript{f}A negative value for \( \hat{\mu}(H) \textsubscript{L} \) implies a polarization of charge which would increase the HAH angle.

\textsuperscript{g}A negative value for \( \hat{\mu}(H) \textsubscript{H} \) implies a polarization of charge which would increase the AH interatomic distance.
contrast to the shapes of the surfaces in $\text{H}_2\text{O}$ and $\text{NH}_3$ are those in $\text{BeH}_2$ and $\text{BH}_3$, where the surfaces bend toward and tightly envelop both the Be and B nuclei. This behaviour of $S(r)$ reflects the depletion of electronic charge in the A fragments of these two molecules. (The net charges of the Be and B fragments at the equilibrium geometries of $\text{BeH}_2$ and $\text{BH}_3$ are 1.723 and 2.137, respectively, indicating a loss of most of the valence charge density in these fragments.)

Properties of the charge distribution within the H fragments, including the fragment populations, are gathered in Table 4.3. From the changes in the H fragment populations, it is seen that on bending both $\text{H}_2\text{O}$ and $\text{NH}_3$ from their respective linear and planar structures (a stabilizing structural change) charge is transferred from the A fragments into the H fragments. When subjected to a similar bending (a destabilizing structural change), the direction of charge transfer in both $\text{BeH}_2$ and $\text{BH}_3$ is just the opposite, i.e., from the H fragments into the A fragments. The relationship between the energy and these observations concerning the direction of charge transfer will be discussed in the following section.

It was shown in Chapter 2 that quantitative information about the distribution of charge within a fragment can be gained from a knowledge of the electronic force and dipole moment vectors associated with the fragment. Such quantities
have been calculated for the H fragments on the molecules now under consideration. For the present purposes \( \hat{u}(H) \) and \( \hat{F}_H(H) \) have been broken up into parallel and perpendicular components with respect to the A-H internuclear axis. These components are denoted by the subscripts || and \( \perp \) respectively. The quantity \( \hat{F}_H(H)_{||} \) represents the force exerted on the proton by the charge density within the H fragment and directed parallel to the A-H axis. A positive value for this quantity implies an antibinding force on the proton, i.e., a force tending to increase the A-H separation. A negative value for \( \hat{u}(H)_{\perp} \) as well as a positive value of \( \hat{F}_H(H)_{||} \) indicates charge accumulation on the non-binding side of the hydrogen fragment. The quantity \( \hat{F}_H(H)_{\perp} \) is the component of \( \hat{F}_H(H) \) directed at right angles to the A-H internuclear axis. The sign convention is such that if \( \hat{F}_H(H)_{\perp} > 0 \) and \( \hat{u}(H)_{\perp} < 0 \) charge density is polarized in a manner favouring an increase in the H-A-H angle.

Numerical values for these vectors are collected in Table 4.3.

In the linear and planar geometries of these molecules the symmetry of the charge distributions dictates a value of zero for the perpendicular components of both the force and the dipole vectors. On bending, this symmetry constraint is lost so that any imbalance of charge density across the A-H bond axis becomes manifest in the signs and magnitudes of \( \hat{u}(H)_{\perp} \) and \( \hat{F}_H(H)_{\perp} \). At the stable equilibrium geometry of both \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) the positive and negative signs of \( \hat{u}(H)_{\perp} \) and \( \hat{F}_H(H)_{\perp} \) respectively suggest the presence of charge accumulation in...
the binding region* of each molecule. Compare these results with those found for the bent and pyramidal forms of BeH₂ and BH₃ respectively. The signs of \( \mu(H) \) and \( \mu(H) \) each indicate that charge has been removed from the binding regions in these molecules. Thus, bending the linear H₂O molecule or the planar NH₃ molecule induces a flow of charge into the binding region which, in turn, exerts forces on the nuclei to enhance further bending. On bending BeH₂ or BH₃ from their stable linear and planar geometries respectively charge density redistributes itself in a manner which creates forces on the nuclei to oppose further bending.

The interpretation of the parallel components of the force and dipole moment vectors is not as straightforward as their perpendicular counterparts. Changes in the quantities \( F_{\parallel}(H) \) and \( \mu(H) \) reflect changes in the distribution of charge across the plane through the proton and perpendicular to the A-H axis. From the data in Table 4.3 it is seen that for all the molecules except H₂O, there is a binding force on the proton exerted by the charge density of the hydrogen fragment. (The antibinding force present in H₂O is a consequence of the close proximity

* The binding region is defined as that region in which an element of electronic charge exerts forces on the nuclei in a direction such that they would decrease all internuclear distances. For the C₂ᵥ and C₃ᵥ structures of the molecules considered here, the region of space within the triangle and the pyramid formed by the nuclei is included in the binding region. The region above the A nucleus in these structures is not included and, consequently, constitutes a non-binding region, i.e., a region in which charge exerts forces on the nuclei which would cause an increase in at least one or more internuclear separations.
of the proton to the zero-flux surface bounding the fragment (cf. Figure 4.1). For both \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) changes in the relative magnitudes of \( \nabla_p (\text{H})_H \) indicate a build up of charge density in the binding region of the \( \text{H} \) fragment when these molecules are bent from their linear and planar geometries respectively. Just the opposite behaviour is observed for \( \text{BeH}_2 \) and \( \text{BH}_3 \). Bending these molecules from their equilibrium geometries causes charge to be removed from the binding region of the \( \text{H} \) fragments.

There is a growing body of numerical evidence suggesting that internuclear null points (points in \( \nabla_p (\text{r}) \) where \( \nabla_p (\text{r}) = 0 \) are physically meaningful points within the charge distribution. Apart from those paths of \( \nabla_p (\text{r}) \) which, collectively, compose the zero-flux partitioning surfaces, there are two (and only two) other paths of \( \nabla_p (\text{r}) \) which emanate from an internuclear null point. These particular paths follow the ridge of maximum density between two "bonded" nuclei and terminate at said nuclei. As they always trace out the line of maximum charge density between nuclei, these paths of \( \nabla_p (\text{r}) \) define, what will be termed, "bond paths" in a molecular system. For any internuclear axis coincident with a symmetry axis the null point will lie on the axis and the bond path traced out by \( \nabla_p (\text{r}) \) will be colinear with the internuclear axis. However, in those cases where the internuclear axis does not coincident with an axis of symmetry, the internuclear null point will not, in general, lie on the axis and the bond path joining the
two nuclei will deviate from the internuclear axis. This is the physical basis for the concept of "bent bonds" (67).*

At the equilibrium geometries of \( \text{H}_2\text{O} \) and \( \text{NH}_3 \), the O-H and N-H internuclear null points are displaced off the bond axis toward the inner region of the molecule by amounts of 0.0062 au and 0.0058 au respectively. Thus the bond paths in these molecules are inwardly curved. In contrast, the A-H bond paths in the \( C_{2v} \) form of \( \text{BeH}_2 \) and the \( C_{3v} \) form of \( \text{BH}_3 \) are curved out; the null points lie 0.142 au and 0.109 au respectively off the internuclear axis.

The bond path, by definition, follows the ridge of maximum density, thus its displacement off the bond axis is itself an indicator of the readjustment of charge density which takes place following a change in molecular structure. Descriptions of the charge distribution inferred by the signs of the vectors \( \Phi_{\text{H}}(\text{H}) \) and \( \mu(\text{H}) \) are substantiated by the shape of the bond paths - or more precisely, by the displacement of the internuclear null point. The curving out of the bond paths in the bent and pyramidal forms of \( \text{BeH}_2 \) and \( \text{BH}_3 \) respectively signifies the outward shift in their charge densities; a shift which destabilizes these molecules by introducing electrostatic forces which oppose the bending process. Similarly, the inward curvature of the bond paths in both the \( C_{2v} \) form of \( \text{H}_2\text{O} \) and the

*The most noted example of a "bent bond" is probably the C-C bond in cyclopropane (67). The null point between the carbons in this molecule lies outside the ring at a distance of 0.11 au from the bond axis (84). Cyclopropane is representative of most small saturated ring systems (5-membered rings or less) in that the null point will lie outside the ring.
\( C_{3v} \) form of \( \text{NH}_3 \) indicate the stability of these structures.* Thus, information paralleling the relaxation of \( \rho(r) \) caused by a change in the bond angle, whether it facilitates or retards such a motion, is built into the static charge distribution as determined by the position of the internuclear null points.

(D) **Partitioning Results: Energy Partitioning**

The underlying process which provides the impetus for the reorganization of electronic charge accompanying a change in the nuclear framework is the drive toward a minimum in the total energy. Having described the major effects of molecular bending upon the charge distributions of \( \text{BeH}_2, \text{BH}_3, \text{NH}_3 \) and \( \text{H}_2\text{O} \), this section deals with the changes in fragment energetics and their relationship to the aforementioned changes in the charge distribution.

In general, the energy of a fragment is affected by both population changes and charge reorganization, including a net

---

*Bent bonds have traditionally been associated with "strains" inherent in the molecular structure (69) and, indeed, strain energies have been proposed and calculated (67). The concept of molecular strain can be related directly to properties of the charge distribution — notably, the positions of the null points. For example, in the highly strained cyclopropane molecule the ring of maximum density is curved out, thereby creating an electrostatic environment conducive to ring opening. These arguments can also be extended to include the concept of "aromatic stability". In benzene, one of the most stable of ring compounds, the null points between the carbons lie inside the ring. Charge density in benzene has accumulated within the ring and, consequently, exerts an inward or binding force on the nuclei forming the ring.*
expansion or contraction of the charge density. For the fragment \( \Omega \), a decrease in its population or a net expansion of its charge density will cause both the average electron-nuclear attraction energy, \( V'(\Omega) \), and the average electron-electron repulsion energy, \( V''(\Omega) \), to decrease in magnitude; similarly, both of these functions will increase for either an increase in population or a net contraction of the charge density. For example, on bending the BeH\(_2\) molecule to its linear zero-force geometry, the quantities \( |V'(\text{Be})| \) and \( V''(\text{Be}) \) both increase despite a loss of charge from the Be fragment. In this case the energy changes occurring in the Be fragment are governed primarily by a net contraction of this fragment's charge density. In addition to its effect on the quantities \( V'(\Omega) \) and \( V''(\Omega) \) a fragment charge distribution contracted toward the nuclear center contained within the fragment causes, on average, a unit electronic charge to be more strongly bound to the nucleus. For the variational fragment \( \Omega \) the binding per electron is expressed as the ratio \( V'(\Omega)/\bar{N}(\Omega) \). In the above example, the one-electron binding energy of the Be fragment increases in magnitude from 14.21 au/e\(^-\) to 14.34 au/e\(^-\) during the bending process. Since the decrease in \( \bar{N}(\text{Be}) \) for this same process is small, the increase in binding per electron dominates the potential energy changes.

The results of energy partitioning together with the energy changes (corresponding to the stabilizing structural transition) between the two geometries for each molecule
appear in Table 4.4. The $\text{H}_2\text{O}$ molecule is most stable at the $\text{C}_{2v}$ geometry. A look at the fragment total energies in $\text{H}_2\text{O}$ reveals that the greater stability of the $\text{C}_{2v}$ form over the linear form of the molecule is the increased stability of the hydrogen fragments. On bending the water molecule from its linear, zero-force geometry each $\text{H}$ fragment becomes more stable by 58.9 kcal/mole, while the oxygen fragment during this process undergoes a decrease in stability amounting to 77.8 kcal/mole.

The lower energy of the $\text{H}$ fragment in the $\text{C}_{2v}$ form of $\text{H}_2\text{O}$ results solely from decrease in the electron-nuclear attractive potential energy; the other potential energy terms, $\nabla''(\text{H})$ and $\nabla_\text{H}(\text{H})$, both increase and, hence, act to destabilize the $\text{H}$ fragments. Although electron-nuclear attractions increase in the $\text{H}$ fragment they decrease in the $\text{O}$ fragment and result in this fragment's increased total energy in the equilibrium geometry of $\text{H}_2\text{O}$. The decrease in $|\nabla'(\text{O})|$ is partially offset by reductions in the repulsive potential energies — particularly $\nabla''(\text{O})$, the electron-electron repulsion energy of the $\text{O}$ fragment.

The fragment energy changes just described between the two structures of $\text{H}_2\text{O}$ vary in accordance with the direction of charge transfer between the $\text{O}$ and $\text{H}$ fragments (charge is transferred from (O) to (H)). The increased population of the hydrogen fragments causes an increase in the average electrostatic interactions within these fragments. Such increased
Figure 4.2

Density difference plots\textsuperscript{a} for H\textsubscript{2}O (A) and BeH\textsubscript{2} (B) showing the changes in $\rho(r)$ which accompany a small decrease in the HAH angle from an initial value of 180\textdegree. In each plot the position of A nucleus is fixed.

Plot A: $\Delta \rho(r)$ for H\textsubscript{2}O

$$\Delta \rho(r) = \rho(r) - \rho(173.5, 180.0)$$

Plot B: $\Delta \rho(r)$ for BeH\textsubscript{2}

$$\Delta \rho(r) = \rho(r) - \rho(174.5, 180.0)$$

\textsuperscript{a}The dashed contours represent regions for which $\Delta \rho(r)$ is negative. The solid contours represent regions for which $\Delta \rho(r)$ is zero or positive. The values of the contours (in au) are incremented in steps of 0, ±0.002, ±0.004, ±0.008, ±0.02,..... to a limit of ±20.
interactions are, in turn, reflected in the increased magnitudes of the potential energy functions, $V'(H)$, $V''(H)$ and $V_n(H)$. Similarly, the oxygen fragment, having lost electronic charge, experiences a decrease in the magnitudes of its potential energy components.

Detailed information concerning the relationship between the changes of the charge distribution occurring within a fragment and the corresponding fragment energy changes can be gained with aid of a variant of a charge density difference map. Diagram A of Figure 4.2 illustrates density differences between two slightly different geometries of the $H_2O$ molecule. In this diagram the oxygen nuclei have been superimposed and the contours represent $\Delta \rho(r)$ where $\Delta \rho(r) = \rho(r) - \rho_r(r)$ and the subscripts refer to the value of 175.5 180.0 the H-O-H angle. (Only the contours in a region approximated by that of the O fragment are particularly meaningful. Those contours about the H nuclei merely reflect the translation in position of these nuclei.) The area of the map contained within the O fragment shows changes in the charge distribution accompanying a small structural change from a linear geometry. The dashed contours in the non-binding region of the O fragment show that charge density has been removed from this region in the bent form of the molecule. Further, charge has accumulated in the binding region of (O). Thus, on bending the $H_2O$ molecule from a linear geometry to a more stable $C_{2v}$ geometry there is charge transfer, not only from the O to the H fragments, but
from the non-binding to the binding region of the O fragment.

The corresponding energy changes of the O fragment include a decrease in the magnitudes of both $\nabla''(O)$ and $\nabla'(O)$ as well as an increase in the magnitude of $\nabla'(O)/N(O)$, the one-electron binding energy in the O fragment. In terms of $\Delta \rho(r)$, then, the stabilizing reductions in the average electron-electron repulsive interactions stems from the removal of charge from the non-binding region of the O fragment. Secondly, although the electron-nuclear attractive interactions decrease in magnitude as a result of the transfer of charge from (O) to (H), the accompanying reorganization of the charge density in (O) increases the binding per electron in the O fragment. Thus, the accumulation of charge in the binding region, as illustrated in Figure 4.2, minimizes the destabilizing change in $\nabla'(O)$ caused by the charge transfer out of the fragment.

BeH$_2$, in contrast to H$_2$O, is most stable as a linear molecule. (In keeping with the present convention of considering stabilizing changes in geometry the energetics associated with bending BeH$_2$ from its unstable C$_{2v}$ form to its equilibrium linear structure will be analysed.) From the data in Table 4.4 it is seen that both the H and Be fragments are more stable in the linear structure as compared to the C$_{2v}$ form of the molecule. The greater stability of the H fragments is due to a decrease in the electron-electron repulsion energy plus an increase in the magnitude of the electron-nuclear attraction energy. The change in $\nabla'_n(H)$, the nuclear virial, is destabil-
izing. Increased stability of the Be fragment arises, in part, from an increase in the magnitude of $\nabla'(\text{Be})$ but is primarily a result of a decrease in the nuclear virial of the Be fragment.

The Be fragment in BeH$_2$ is characterized by a decreasing population as well as a net contraction of its charge density during the stabilizing structural change from the bent to the linear form of the molecule. The overall effect on the energy of (Be) is an increase in the values of both $|\nabla'(\text{Be})|$ and $\nabla''(\text{Be})$. As was pointed out early in this section, the direction of these potential energy changes indicates the predominance of charge contraction over population changes in governing the energetics of the Be fragment.

The specific pattern of charge redistribution in (Be) for a small variation in the bending mode of BeH$_2$ is obtained from a $\Delta \rho(r)$ map analogous to that used previously for the H$_2$O molecule. Diagram B of Figure 4.2 shows the changes in $\rho(r)$ which take place in the Be fragment accompanying a $5.5^\circ$ change in the H-Be-H angle. The contours represent $\Delta \rho(r)$ where $\Delta \rho(r) = \rho(r) - \rho_0(r)$. (Note that the maps for both H$_2$O and BeH$_2$ in Figure 4.2 correspond to a structural change from linearity. For BeH$_2$ this is a destabilizing structural change.) A comparison of the $\Delta \rho$ maps for H$_2$O and BeH$_2$ immediately reveal basic differences in the bending mode of these two molecules. The most striking difference is the opposite direction of charge flow within the central fragment. On bending the BeH$_2$ molecule from its linear equilibrium geometry electronic charge is
induced into the non-binding region of the central fragment, as opposed to being removed from this region, as is the case for the \( \text{H}_2\text{O} \) molecule.

The charge which is induced into the non-binding region of the \( \text{BeH}_2 \) molecule is removed from the binding regions of both the \( \text{Be} \) and \( \text{H} \) fragments. The major effect of this re-organization of charge on the energy is a destabilizing reduction in the magnitude of the average electron-nuclear attraction energy in each of the \( \text{Be} \) and \( \text{H} \) fragments — particularly in the \( \text{H} \) fragments.

The pattern of energy changes recorded in Table 4.4 for the virial fragments of \( \text{NH}_3 \) parallel those of the \( \text{H}_2\text{O} \) molecule. \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) become more stable on bending from their respective linear and planar zero-force geometries. In each case increased molecular stability arises from a local stabilization of the \( \text{H} \) fragments caused by increases in the magnitude of \( \nabla''(\text{H}) \), as well as stabilizing decreases in the repulsive interaction energies of the \( \text{A} \) fragment, \( \nabla''(\text{A}) \) and \( \nabla''(\text{A}) \). The predominant factor underlying the fragment energy changes in both \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) between their respective zero-force geometries is the change in population of these fragments resulting from the charge transfer between \( \text{(A)} \) and \( \text{(H)} \) (charge transfer is from \( \text{(A)} \) to \( \text{(H)} \) for the stabilizing structural change). That the variations in the magnitude of the fragment energies in \( \text{NH}_3 \) are smaller than those in \( \text{H}_2\text{O} \) is consistent with the smaller amount of charge transfer in \( \text{NH}_3 \) than in \( \text{H}_2\text{O} \).
A parallelism similar to that observed in the energy changes of H$_2$O and NH$_3$ is present to some extent in the energetics of the BeH$_2$ and BH$_3$. The greater stability of both the planar structure of BH$_3$ and the linear structure of BeH$_2$ over their respective C$_3v$ and C$_2v$ structures is due largely to an increased magnitude of the electron-nuclear attraction energy in the H fragments, V'(H). As well, the reorganization of charge within the A fragments is such that the binding per electron in these fragments is increased in the equilibrium geometries of both molecules.

Differences in the patterns of fragment energy changes for BeH$_2$ and BH$_3$ stem from the relative differences in the magnitude of charge transfer in these two molecules. Although the direction of charge transfer is the same, the fragment population changes in BH$_3$ are nearly six times as great as those in BeH$_2$ (ΔN(H) in BH$_3$ = 0.058 e$^-$ and ΔN(H) in BeH$_2$ = 0.010 e$^-$). Consequently, the changes in the fragment energies of BH$_3$ are governed primarily by their changes in population, whereas in BeH$_2$ the fragment energies are more influenced by the reorganization of charge which takes place within the fragments.

(E) Summary

It is observed that the changes in the molecular charge and energy distributions accompanying changes in geometry of the AH$_n$ series of hydrides are characterized by the presence or absence of non-bonded valence electrons in the A fragment of the molecule undergoing the change. For both the H$_2$O and
NH₃ molecules, molecules having non-bonded valence electrons, the increased stability of their respective bent and pyramidal structures is due to net decreases in the molecular repulsion energies, Ψ'' and Ψn. A breakdown of the molecular energy changes into localized contributions from virial fragments shows that the decreases in Ψ'' and Ψn in both H₂O and NH₃ are a result of decreases in the repulsion energies of the O and N fragments, that is, decreases in the quantities Ψ''(A) and Ψn(A) where A = O or N. An analysis of the changes in the charge distribution subject to a variation in the H-O-H of H₂O reveals that the decreases in the repulsive energies of (O) occur as a result of a removal of charge from the non-binding region* of this fragment. Further, the charge which is removed from the non-binding region in (O) is transferred: (1), into the H fragments where molecule stabilization is enhanced by the increase in the magnitude of the electron-nuclear attractions in these fragments (Ψ'(H)), and (2), into the binding region of the central fragment where its accumulation acts to minimize the destabilizing change in Ψ'(O) caused by the charge transfer out of the fragment. The inherent stability of the C₂ᵥ and C₃ᵥ structures of H₂O and NH₃ respectively is built into their static charge distributions and is reflected by the inward curvature of the bond paths in these structures.

*The non-binding regions of the O and N fragments of H₂O and NH₃ correspond roughly to the region of space thought of as being occupied by the lone pair electrons of these molecules. That electron repulsions in this region are reduced, and further, that they are reduced more so in the O fragment than in the N fragment by molecular bending is in accord with the qualitative arguments of the VSEPR (Valence shell electron-pair repulsion) model of molecular geometry(70,71).
The BeH$_2$ and BH$_3$ molecules, molecules characterized by the absence of non-bonded valence electrons, are more stable at their respective linear and planar geometries than their corresponding bent and pyramidal geometries. The increased molecular stability is achieved through net increases in the magnitude of the electron-nuclear attraction energy ($|V'|$) in these two molecules. The increases in $|V'|$ occur primarily as a result of charge transfer into and subsequent increases in the magnitude of the electron-nuclear attraction energy of the H fragments. In the less stable bent and pyramidal forms of BeH$_2$ and BH$_3$ respectively, charge is accumulated in the non-binding region of the A fragments. (This is in direct contrast to that which takes place in the corresponding and stable structures of H$_2$O and NH$_3$.) Accordingly, the structural instability associated with the C$_{2v}$ and C$_{3v}$ forms of BeH$_2$ and BH$_3$ respectively is reflected in their charge distributions as outwardly curving bond paths.
CHAPTER 5

MOLECULAR FRAGMENTS AND THE ELECTROSTATIC POTENTIAL

(A) Introduction.

The potential energy $V_{ij}$ between two discrete charges $q_i$ and $q_j$ is expressed as the quantity $q_i q_j / r_{ij}$, where $r_{ij}$ is the distance between the two charges. If, instead of point charges, $q_i$ and $q_j$ represent two elements of a continuous charge distribution, $\rho(r)$, then the expression for the potential energy between the two elements of charge becomes

$$V_{ij} = \rho(r_i) dr_i \rho(r_j) dr_j / r_{ij}.$$  (5.1)

Consider the interaction between $\rho_a(r)$ and $\rho_b(r)$, two separated and non-overlapping molecular charge distributions. The classical potential energy* of interaction, $V_{ab}$, in this system is obtained by summing the interaction energies between all possible pairs of charges in the two molecules, i.e.,

$$V_{ab} = \int \int (\rho_a(r_i) \rho_b(r_j) / r_{ij}) dr_i dr_j.$$  (5.2)

An important special case of equation (5.2) occurs if one of the two charge distributions is replaced by a unit point charge. The quantity $V_{ab}$ then becomes the interaction energy between a molecular charge distribution and an external point charge. The electrostatic potential, $\phi$, at the point $r_j$, the position of the unit charge, due to the interaction with the

*If the two molecular systems are sufficiently separated there is no exchange contribution to the energy so that the quantum mechanical interpretation is equivalent to the classical.
neighbouring charge distribution is defined according to the equation
\[ \phi(r_{ij}) = \int \frac{\rho(r_i)}{r_{ij}} \, dr_i \quad (5.3) \]
and is the potential energy per unit charge.

In recent years the utility of the molecular electrostatic potential as an interpretive chemical tool has been repeatedly demonstrated (72-75). The most common and probably the most valuable means of analysis of \( \phi(r) \) is through a graphical representation obtained by plotting isopotential curves in selected planes. Such a treatment allows one to view the electrostatic potential surface describing the interaction of a molecule with a unit charge. Thus, for example, electrostatic potential maps are of particular value in the study of protonation reactions (74, 76). In general, these maps may be used as a means of determining the location of reactive sites within a molecule and, as a result, in the elucidation of the chemical reactions of large molecules, particularly those of biological importance (75, 77). (The interaction energy with a point charge \( q \), given by \( q \phi \), is rigorously the first-order perturbation energy of a molecule in the field of that point charge.)

From the equation (5.3) it is seen that the calculation of \( \phi(r) \) at a single point involves an integration over the complete charge distribution. Hence, an accurate map of the potential surface necessitates the calculation of \( \phi(r) \) at a large number of points on the surface; consequently, the generation of these maps can often consume a great deal of
computer time — especially when using a wavefunction described by a large basis set. In order to overcome this practical difficulty, methods other than the direct application of equation (5.3) have been proposed\(^{78,79}\). Of these, a form of the multipole moment expansion method\(^{79}\) is further investigated in this work.

The multipole moment expansion method expresses the electrostatic potential as a series expansion of the form

\[
\phi(\mathbf{r}) = \sum_{\ell=0}^{\infty} \phi_{\ell}(\mathbf{r})
\]  

(5.4)

where each term in the series is related to a particular multipole moment of the charge distribution, i.e., \(\phi_{0}(\mathbf{r})\) relates to its monopole, \(\phi_{1}(\mathbf{r})\) to its dipole, etc. Clearly, the usefulness of equation (5.4) as a means to approximate \(\phi(\mathbf{r})\) is dependent upon its rate of convergence. A one-center expansion, that is, an expansion based on multipole moments describing the total molecular charge distribution, is noted to have a relatively slow convergence\(^{80}\) (moments of higher order than the octupole need to be included in equation (5.4) in order to obtain a reliable estimate of the potential surface). If, instead, a multi-center expansion is used, considerable improvement in the speed of convergence is achieved\(^{80}\). The most convenient of the multi-center expansions is the N-center expansion where N represents the number of nuclei in the system\(^{80}\). By virtue of an expansion at each nuclear center, the N-center expansion method necessitates that atomic analogues of the multipole moments be defined for each center. These quantities
have generally been obtained via a mathematical partitioning of elements in the first-order density matrix\(^{(80)}\). The atomic moments obtained in this fashion suffer from some degree of arbitrariness (cf. the footnote at the bottom of page 48 regarding atomic populations). The Virial Partitioning Theory, on the other hand, not only allows the fragment moments to be unambiguously defined, but provides a set of moments which are physically meaningful in that they approximate the potential generated by the charge distribution contained within a well-defined region of real space.

Using fragment moments which relate directly to localized distributions of charge has the important added advantage that a characterization of the total electrostatic potential map in terms of the charge distribution and properties of the component fragments is possible. Thus, for example, the effect on the potential field from specific functional groups within the molecule may be studied.

An important and natural extension of the multipole moment expansion method concerns the question of transferability of functional groups. The Virial Partitioning Theory naturally accounts for any transferability of fragment properties. From a judicious choice of a number of small molecules, a compilation of characteristic fragment moments can be obtained. Through the use of such a collection of multipole moments the potential fields of large molecular systems could be generated quickly and without the use of wavefunctions.
(B) **Derivation of the Multipole Moment Expansion Approximation**

A charge \( q \) at the point \( r_q \) in the vicinity of a localized charge distribution will feel a force according to the equation

\[
\vec{F}(r_q) = q \int (\rho(r)(\vec{r}_q - \vec{r})/|\vec{r}_q - \vec{r}|^3) \, d\vec{r}
\]

(5.5)

where the vectors \( \vec{r}_q \) and \( \vec{r} \) are defined in Figure 5.1.

![Figure 5.1](image)

The electric field, \( \vec{E} \), at a point is related to the force exerted on a charge at that point in the limit as the charge approaches zero. At the point \( r_q \) the electric field therefore is given by

\[
\vec{E}(r_q) = \lim_{q \to 0} \frac{\vec{F}(r_q)}{q} = \int \rho(r) \frac{(\vec{r}_q - \vec{r})}{|\vec{r}_q - \vec{r}|^3} \, d\vec{r}
\]

(5.6)

Of fundamental importance to the development of potential theory is the concept of a conservative vector field.* It is this conservative property of the electrostatic vector field which allows one to write an equation of the form

---

* A vector field \( \vec{A} \) is conservative if for all points within the field the curl of the vector is zero, i.e., \( \nabla \times \vec{A} = 0 \). Physically this corresponds to the vector field having no circulation or vorticity. The consequence of a conservative field is the existence of a scalar function, \( \phi \), which is related to the vector field by the relation \( \vec{A} = \nabla \phi \).
\[ \mathbf{E}(\mathbf{r}) = -\nabla \phi(\mathbf{r}) . \] (5.7)

The function \( \phi(\mathbf{r}) \) as defined in the above equation is termed the electrostatic potential. Recalling that \( \nabla(1/|\mathbf{r}_q - \mathbf{r}|) = (\mathbf{r}_q - \mathbf{r})/|\mathbf{r}_q - \mathbf{r}|^3 \), the analytical form of \( \phi(\mathbf{r}) \) in terms of the charge density can be obtained directly from equation (5.6). The result will be a form equivalent to that given previously in equation (5.3).

Strictly speaking, electrostatic potential maps are valid only at large distances from the molecular charge distribution.* In the subsequent development it will be assumed that \( \mathbf{r}_q \), the position of the point charge \( q \), remains outside the charge distribution as determined by the 0.002 au charge density contour; a region within which 98 to 99% of the total charge is contained \(^{28}\).

A series expansion for \( \phi(\mathbf{r}) \) follows directly from the one-center expansion of \( 1/|\mathbf{r}_q - \mathbf{r}| \). If \( (\mathbf{r}_q, \theta_q, \phi_q) \) and \( (\mathbf{r}, \theta, \phi) \) represent the spherical coordinates of the points \( \mathbf{r}_q \) and \( \mathbf{r} \) respectively (see Figure 5.1), then in terms of the associated legendra polynomials, \( P_n^m(\cos \theta) \), the expansion of \( 1/|\mathbf{r}_q - \mathbf{r}| \) takes the form

\[
\frac{1}{|\mathbf{r}_q - \mathbf{r}|} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{(n-m)!}{(n+m)!} \frac{r^n}{r_q^{n+1}} P_n^m(\cos \theta) P_n^m(\cos \theta_q) e^{im(\phi - \phi_q)} \] (5.8)

* \( \rho(\mathbf{r}) \) in equation (5.3) is the unperturbed charge distribution for the isolated molecule. Clearly, the approach of a charged species will induce charge polarizations in the molecule thereby perturbing the ground state distribution. This, in turn, alters the potential surface. At large \( \mathbf{r} \), the interaction between molecule and ion is small and consequently charge polarization effects are minimal.
Upon substitution of equation (5.8) into (5.3) one obtains the following expression for \(\phi(r_q)\):

\[
\phi(r_q) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{(n-m)!}{(n+m)!} q_n^m p_n^m (\cos \theta_q) e^{-i m \phi_q} \int r_q^{n+1} \rho(r) r^n p_n^m (\cos \theta)e^{im\phi} dr.
\]

(5.9)

where

\[
q_n^m = \int r_q^{n+1} \rho(r) r^n p_n^m (\cos \theta)e^{im\phi} dr.
\]

(5.10)

The set of \(q_n^m\) values may be considered as coefficients in the expansion of equation (5.9) and correspond only to the properties of the charge distribution. They are directly related to the multipole moments of the system and, as a result, equation (5.9) can be reformulated as

\[
\phi(r_q) = \phi_0(r_q) + \phi_1(r_q) + \ldots.
\]

(5.11)

where \(\phi_0(r_q)\) represents the monopole contribution to the potential, \(\phi_1(r_q)\) the dipole contribution, and so on. Each of the terms of the expansion in equation (5.11) can be written explicitly in terms of the multipole moments describing the charge distribution — once these moments have been defined. In this work the first three moments are defined as follows: the monopole and dipole moments, \(c\) and \(\vec{u}\), respectively, are expressed in the usual manner, i.e., \(c = \int \rho(r) dr\) and \(\vec{u} = \int \rho(r) \vec{r} dr\). In defining the quadrupole moment in a cartesian reference system, some arbitrariness is possible since only 5 of the 6 cartesian components are independent. The definition adopted here is that used by Hirschfelder, Curtiss and Bird (4), that is, the
quadrupole moment is defined as a traceless tensor whose components are

$$Q_{x_i x_j} = \int \rho(r) \left( 3 x_i x_j - r^2 \delta_{ij} \right) dr$$  \hspace{1cm} (5.12)

where \(x_1 = x, x_2 = y, x_3 = z\) and \(\delta_{ij}\) is the kronecker delta.

The explicit form of equation (5.11) in terms of the multipole moments as defined above becomes

$$\phi(r_q) = \frac{c}{r_q} + \frac{\mu \cdot \vec{r}}{r_q^3} + \frac{\Sigma_{i,j} Q_{x_i x_j} x_i x_j}{r_q^5} + \ldots$$  \hspace{1cm} (5.13)

For the important special case of a cylindrically symmetric charge distribution equation (5.13) reduces to

$$\phi(r_q) = \frac{c}{r_q} + \frac{\mu_z z_q}{r_q^3} + \frac{Q_{zz} (3z_q^2 - r_q^2)}{4r_q^5} + \ldots$$  \hspace{1cm} (5.14)

where the axis of symmetry is taken as the z axis.

Equation (5.14) represents a one-center expansion. The multipole moments describe the total charge distribution. The extension to a multi-center expansion is straightforward. If the molecule is partitioned into its monatomic fragments, each with its own set of multipole moments, the RHS of equation (5.13) need only be summed over all fragments of the system. Thus, for a charge distribution containing \(N\) nuclear centers

$$\phi(r_q) = \sum_{\omega} \left[ \frac{\bar{c}(\omega)}{r_q} + \frac{\bar{\mu}(\omega) \cdot \vec{r}}{r_q^3} + \frac{\Sigma_{i,j} Q_{x_i x_j} (\omega) x_i x_j}{r_q^5} + \ldots \right]$$  \hspace{1cm} (5.15)
where each of the multipole moments describe the charge distribution associated with the fragment $\Omega$.

In the preceding development the nuclear charges have been implicitly treated as part of $\rho(r)$, the charge density. The nuclear contribution to the electrostatic potential, $\phi_n(r_q)$, is given by the expression

$$\phi_n(r_q) = \sum_{\Omega}^{N} \frac{Z_{\Omega}}{r_q}$$

(5.16)

($Z_{\Omega}$ is the charge on the nucleus within the fragment $\Omega$) and is totally incorporated into $\phi_0(r_q)$, the monopole term of the expansion.

(C) The Electrostatic Potential and Fragment Moments

As an aid to analyzing the many features of an electrostatic potential map, it is helpful to have some knowledge of the characteristic fields which result from the superpositions of moments on different centers. Figure 5.2 shows several plots of the potential fields obtained from assumed dipole and quadrupole fragment moments in a diatomic system. Down the left hand column are plots of $\phi(r)$ obtained from the addition of two dipole fields of varied magnitude and direction. Denoting the diatomic molecule as AB, the plots A, C, E and G represent fields for which $\hat{\mu}(A) = \hat{\mu}(B)$, $\hat{\mu}(A) = 2\hat{\mu}(B)$, $\hat{\mu}(A) = -2\hat{\mu}(B)$ and $\hat{\mu}(A) = -\hat{\mu}(B)$, respectively. The potential fields generated from the superposition of two quadrupole moments are shown in the plots B, D, F and G in which $Q_{zz}(A) = Q_{zz}(B)$,
Figure 5.2

Model potential fields derived from assumed values for atomic dipole\textsuperscript{a} and quadrupole moments of a diatomic molecule AB. Dashed contours represent regions of negative potential. The relative values for the atomic moments to generate the plots are given below.

Plot A: $\vec{\mu}(A) = \vec{\mu}(B)$
Plot B: $Q_{zz}(A) = Q_{zz}(B)$
Plot C: $\vec{\mu}(A) = 2\vec{\mu}(B)$
Plot D: $Q_{zz}(A) = 2Q_{zz}(B)$
Plot E: $\vec{\mu}(A) = -2\vec{\mu}(B)$
Plot F: $Q_{zz}(A) = -2Q_{zz}(B)$
Plot G: $\vec{\mu}(A) = -\vec{\mu}(B)$
Plot H: $Q_{zz}(A) = -Q_{zz}(B)$

\textsuperscript{a}A negative value for $\vec{\mu}$ implies the direction $A^+B^-$. 
Figure 5.3

Molecular electrostatic potential maps\(^{a}\) derived by the multipole moment expansion approximation of equation 5.15.

Plot A: \(\bar{N}_2\)  
Plot B: \(CN\)

Plot C: \(BeF\)  
Plot D: \(BeH\)

Plot E: \(FCN\)  
Plot F: \(CICN\)

\(^{a}\)Dashed contours represent regions of negative potential. The values of the contours (in au) are incremented in steps of: \(\pm 0, \pm 0.002, \pm 0.004, \pm 0.008, \pm 0.02, \ldots \pm 20\).

1 au = 627.71 kcal/mole.
\[ Q_{zz}(A) = 2Q_{zz}(B), \quad Q_{zz}(A) = -2Q_{zz}(B) \quad \text{and} \quad Q_{zz}(A') = -Q_{zz}(B), \]
respectively. In these and in all other maps of \( \phi(r) \) an area within 3 au of any nuclear center has not been plotted. This omitted region corresponds to the approximate boundary of the molecular charge distribution and in which the multipole moment approximation breaks down.

A number of generalizations can be made from the plots in Figure 5.2. The resultant field of two like moments of the same sign and magnitude (plots A and B) is similar in shape to that generated by either of the isolated moments. The potential field resulting from two moments of equal magnitude but of opposite sign corresponds to that produced by the next higher order moment. Thus, for example, plots G and H give rise to quadrupolar and octupolar fields respectively. The remaining plots illustrate fields which are intermediate between the extremes just described, and which often resemble actual molecular potential maps of diatomic molecules. Note that the origins of the resultant fields illustrated in Figure 5.2 are located at the midpoint of AB if the fragment moments are equal in magnitude (plots A, B, G and H) or shifted from the midpoint toward the center possessing the largest moment (largest in magnitude).

Electrostatic potential maps obtained via the multipole moment approximation of equation (5.15) for several linear molecules are shown in Figure 5.3. Terms up to and including the octupole terms were considered in the expansion. Compiled
in Table 5.1 are the corresponding fragment moments for these and other linear molecules.

The potential field of plot A in Figure 5.3, generated by the N₂ molecule, is purely quadrupolar in character. Since there is no charge transfer in N₂, the monopole term in the expansion does not contribute to this field. The N fragment dipole moments are equal in magnitude and opposite in sign; consequently the dipole term contributes a quadrupolar field similar to that of plot G in Figure 5.2. The quadrupole moments of the N fragments are positive and equal in magnitude and hence act to generate a quadrupolar field; one which opposes, however, the quadrupolar field of the dipole term. Although the magnitudes of the quadrupole moments exceed those of the dipole moments, the dipole term dominates the resultant potential field of N₂.* The dominance of the dipole term is due to the fact that it contributes to \( \phi(r) \) through a \( 1/r^2 \) dependence as opposed to the \( 1/r^3 \) dependence of the quadrupole term. By the same token, the octupole and subsequent terms contribute increasingly smaller amounts to \( \phi(r) \). In most cases the qualitative features of a potential surface can be accounted for by the first two non-zero terms of the expansion.

*Notice that in this case the two opposing quadrupolar fields do not add to produce an octupolar field such as that produced in plot H of Figure 5.2. In N₂ the origins of the opposing quadrupolar fields are coincident whereas in the plots of Figure 5.2 the origins are set apart (2 au). In general, when the origins of two (or more) like multipole moment fields are coincident (and their principle axis are colinear), the resultant field will retain the characteristic shape of the individual fields.
Table 5.1

Fragment Moments of Linear Molecules \(^{(e)}\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Monopole (^{(a)})</th>
<th>Dipole (^{(b)})</th>
<th>Quadrupole (^{(c)})</th>
<th>Octopole (^{(d)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>0.9110(^{a})</td>
<td>0.0013</td>
<td>0.0525</td>
<td>0.0029</td>
</tr>
<tr>
<td>LiF</td>
<td>-0.9110</td>
<td>0.3866</td>
<td>1.5265</td>
<td>-0.0807</td>
</tr>
<tr>
<td>BeH</td>
<td>0.8370</td>
<td>0.0167</td>
<td>0.0616</td>
<td>0.0056</td>
</tr>
<tr>
<td>BeF</td>
<td>-0.8370</td>
<td>0.2758</td>
<td>0.7464</td>
<td>-0.0499</td>
</tr>
<tr>
<td>NO</td>
<td>0.9451</td>
<td>0.5714</td>
<td>0.8850</td>
<td>-0.0833</td>
</tr>
<tr>
<td>NO</td>
<td>-0.9450</td>
<td>1.5201</td>
<td>2.8734</td>
<td>0.0028</td>
</tr>
<tr>
<td>CN</td>
<td>0.9451</td>
<td>1.4284</td>
<td>2.0898</td>
<td>-0.0209</td>
</tr>
<tr>
<td>CN</td>
<td>-0.9451</td>
<td>1.5009</td>
<td>0.5500</td>
<td>-0.0563</td>
</tr>
<tr>
<td>CO</td>
<td>0.4951</td>
<td>0.9897</td>
<td>1.5941</td>
<td>0.0866</td>
</tr>
<tr>
<td>CO</td>
<td>-0.4951</td>
<td>0.0410</td>
<td>1.5508</td>
<td>-0.0628</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.3465</td>
<td>1.7009</td>
<td>0.4662</td>
<td>-0.0499</td>
</tr>
<tr>
<td>HCN</td>
<td>1.3464</td>
<td>1.0617</td>
<td>0.0611</td>
<td>-0.0537</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.1233</td>
<td>0.9311</td>
<td>1.5125</td>
<td>0.0812</td>
</tr>
<tr>
<td>HCN</td>
<td>-1.1230</td>
<td>0.5922</td>
<td>0.5531</td>
<td>-0.1109</td>
</tr>
<tr>
<td>HCN</td>
<td>0.0000</td>
<td>0.6199</td>
<td>1.4831</td>
<td>0.1702</td>
</tr>
<tr>
<td>HCN</td>
<td>-0.0000</td>
<td>-0.6199</td>
<td>1.4831</td>
<td>-0.1702</td>
</tr>
<tr>
<td>FCN</td>
<td>0.1527</td>
<td>0.0961</td>
<td>0.3996</td>
<td>0.0097</td>
</tr>
<tr>
<td>FCN</td>
<td>1.2838</td>
<td>1.0512</td>
<td>2.2261</td>
<td>-0.0970</td>
</tr>
<tr>
<td>FCN</td>
<td>-1.4361</td>
<td>0.9132</td>
<td>0.2720</td>
<td>-0.7143</td>
</tr>
<tr>
<td>ClCN</td>
<td>0.7504</td>
<td>-0.5725</td>
<td>0.0582</td>
<td>-0.0701</td>
</tr>
<tr>
<td>ClCN</td>
<td>2.0125</td>
<td>-0.0522</td>
<td>2.9266</td>
<td>0.0449</td>
</tr>
<tr>
<td>ClCN</td>
<td>-1.2617</td>
<td>0.7191</td>
<td>0.8486</td>
<td>-0.1293</td>
</tr>
<tr>
<td>ClCN</td>
<td>0.0000</td>
<td>0.1118</td>
<td>3.9811</td>
<td>-0.0615</td>
</tr>
<tr>
<td>ClCN</td>
<td>1.2965</td>
<td>0.7155</td>
<td>2.6215</td>
<td>0.0007</td>
</tr>
<tr>
<td>ClCN</td>
<td>-1.2930</td>
<td>0.8068</td>
<td>0.5953</td>
<td>-0.1308</td>
</tr>
<tr>
<td>C(_2)O</td>
<td>-1.3789</td>
<td>-0.9379</td>
<td>0.1326</td>
<td>0.0314</td>
</tr>
<tr>
<td>C(_2)O</td>
<td>2.7582</td>
<td>0.0</td>
<td>1.1999</td>
<td>0.0</td>
</tr>
<tr>
<td>C(_2)O</td>
<td>-1.3789</td>
<td>0.9379</td>
<td>0.1326</td>
<td>-0.0314</td>
</tr>
</tbody>
</table>

\(^{a}\)For the molecule AB or ABC the properties of (A) are listed first followed by those of (B), then (C).

\(^{b}\)A negative dipole implies the direction A\(^+\)B\(^-\).

\(^{c}\)Only the \(Q_{xx}\) component is listed. For linear molecules, the off-diagonal elements are zero and \(Q_{xx} = Q_{yy} = -\frac{1}{2}Q_{zz}\).

\(^{d}\)The octopoles are represented by \(Q_{0}^{3}\).

\(^{e}\)All values are in atomic units.
The potential field of the CN molecule, shown in plot B of Figure 5.3, is distinctly dipolar in appearance. This molecule is characterized by a large charge transfer (from (C) to (N)) which acts to produce a strong dipolar field in the same direction as observed in the plot. The effect of the dipole contribution, \( \phi_1 \), is to reduce the strength of the charge transfer field, \( \phi_0 \), by generating a dipolar field of opposite polarity. Again, the lower order term dominates the resultant potential field for reasons given in the previous paragraph.

For the BeF molecule the surrounding potential field has a large degree of quadrupolar character. The shape of this field is markedly different from that of CN in spite of similarities in the fragment moments of these two molecules. In both molecules \( \phi_0 \) contributes a strong dipolar field due to the large charge transfer in these systems, and \( \phi_1 \) acts to weaken this field by contributing a dipolar field of opposite polarity. In a mathematical sense the observed differences in the resultant fields can be explained as follows: because of the larger relative difference in the magnitudes of the fragment dipole in BeF as compared to those in CN, the origin of \( \phi_1 \), the dipole term, is further removed from the bond midpoint in BeF than in CN. Thus the addition of \( \phi_1 \) with \( \phi_0 \) (whose origin is at the bond midpoint in both molecules) produces, in BeF, a resultant field having a larger degree of quadrupolar character than in CN (see plot B of Figure 5.2 together with the footnote on page 122).
Differences in the potential fields of BeF and CN can also be rationalized in terms of differences in their molecular charge distributions. In both the Be and C fragments, charge density is polarized in a direction counter to that of charge transfer; however, the more diffuse valence charge density in the non-binding region of (Be) results in this fragment's greater dipole moment. Hence, the strength of the positive field generated by the positively charged A fragment is reduced to greater degree in BeF than in CN.

In the potential maps of FCN and ClCN notice that the positive region of the electrostatic potential surface is located at the electronegative, F and Cl, ends of the molecule. The shapes of the potential fields surrounding these two molecules are dominated by the monopole contributions of their respective CN groups where a large transfer of charge from (C) to (N) takes place. Note also the near constancy of the potential field about the nitrogen end of the FCN, ClCN and CN molecules. This result is consistent with those in Chapter 2, Section III, which show that the charge distribution and, hence, the properties of the N fragment of the CN group remain relatively unchanged in varied chemical environments.

Consider now the question of accuracy and reliability of the multipole moment expansion method as a means of approximating $\phi(r)$. An illustration of the agreement between the true potential surface and that obtained through equation
(5.15) using multipole moments derived from Virial Partitioning Theory is seen in Figure 5.4 where, for the molecules of LiH, NO and CO, both surfaces are plotted. The approximate potential surfaces, plots A, C and E, were generated using terms up to and including the octupole terms of equation (5.15). The true surfaces were obtained by direct application equation (5.3). Clearly, the basic features of the true potential surfaces are faithfully reproduced by the approximation procedure.

A couple of points merit further comments. An inherent limitation of the multipole moment expansion approximation to \( \phi(r) \) is its inability to reproduce points of relative minima on the potential surface. The location of these points are generally found within the charge distribution as defined by the 0.002 au contour of \( \rho(r) \) and, consequently, are in a region for which equation (5.15) is no longer valid. These points of local minima are important in that they define the depth of the potential wells in which they are situated; a property which may be correlated to proton affinity or reactivity of the corresponding molecules in electrophilic reactions.\(^{(1,5)}\) While the approximate maps of \( \phi(r) \) do not contain these important points, one may still estimate the relative depth of potential wells from the values of the isopotential contours in the region of the local minimum.

The second point concerns the location of
Figure 5.4

A comparison between the molecular electrostatic potential, $\phi(r)$, derived by the multipole moment expansion method (MME) and the corresponding exact potential according to equation (5.3). The maps correspond as follows:

Plot A: LiH $\phi(r)$--MME  Plot B: LiH $\phi(r)$--exact

Plot C: NO $\phi(r)$--MME  Plot D: NO $\phi(r)$--exact

Plot E: CO $\phi(r)$--MME  Plot F: CO $\phi(r)$--exact

\textsuperscript{a}For contour values see caption for Figure 5.3.
the points of relative minima in \( \phi(r) \) as predicted by the approximate maps. For the molecules CO and NO in Figure 5.4, the approximate maps indicate the existence of a double minima on the potential surface at the oxygen end of these molecules. No such double minima is observed on the corresponding exact surface. This behaviour, when it does occur, is most pronounced at O or N sites in a molecule and seems to be a peculiarity of the convergence properties of equation (5.15).

The usefulness of the multipole moment expansion as a means of approximating \( \phi \) depends on its rate of convergence. With the use of multipole moments obtained from a Virial Partitioning of the molecular system, a relatively fast convergence of equation (5.15) is anticipated because (1) the charge density is partitioned in a "natural manner", that is, according to a physically observable property of the charge distribution and (2) the resultant moments are related directly to the spacial distribution of charge within the fragment. Quantitative information concerning the convergence properties of the expansion formula is collected in Table 5.2. Contained in this table is a breakdown into the first four terms of the series expansion at eight specific points about each of the molecules LiF, NO and CO. The particular location of these eight points are shown below in Figure 5.5. Each point is labelled according to whether it lies on the A or B side of the AB molecule and whether it lies 4 or 6 au from the nearest center. Also included in the table is the exact
Table 5.2

Multipole Contributions

to the Electrostatic Potential of LiF, NO and CO.

<table>
<thead>
<tr>
<th>AB</th>
<th>Point</th>
<th>$\phi_0$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>$\phi_{\text{exact}}$</th>
<th>$\Delta \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4</td>
<td>0.0995</td>
<td>-0.0067</td>
<td>0.0016</td>
<td>0.0000</td>
<td>0.0952</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>A'4</td>
<td>0.0458</td>
<td>-0.0066</td>
<td>-0.0029</td>
<td>0.0001</td>
<td>0.0388</td>
<td>-0.0003</td>
<td></td>
</tr>
<tr>
<td>B'4</td>
<td>-0.0458</td>
<td>0.0004</td>
<td>-0.0029</td>
<td>0.0000</td>
<td>-0.0431</td>
<td>0.0052</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>-0.0995</td>
<td>0.0176</td>
<td>0.0059</td>
<td>-0.0002</td>
<td>-0.0794</td>
<td>-0.0032</td>
<td></td>
</tr>
<tr>
<td>LiF Ave$^c$</td>
<td>0.0727</td>
<td>0.0078</td>
<td>0.0027</td>
<td>0.0001</td>
<td>0.0641</td>
<td>0.0024</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>0.0515</td>
<td>-0.0039</td>
<td>0.0007</td>
<td>0.0000</td>
<td>0.0486</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>A'6</td>
<td>0.0161</td>
<td>-0.0027</td>
<td>-0.0003</td>
<td>0.0000</td>
<td>0.0128</td>
<td>-0.0002</td>
<td></td>
</tr>
<tr>
<td>B'6</td>
<td>-0.0161</td>
<td>0.0002</td>
<td>-0.0009</td>
<td>0.0000</td>
<td>-0.0163</td>
<td>0.0005</td>
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</tr>
<tr>
<td>B6</td>
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<td>0.0017</td>
<td>-0.0000</td>
<td>-0.0427</td>
<td>-0.0026</td>
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<tr>
<td>Ave</td>
<td>0.0338</td>
<td>0.0037</td>
<td>0.0009</td>
<td>0.0000</td>
<td>0.0301</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>0.0436</td>
<td>-0.0608</td>
<td>0.0157</td>
<td>-0.0003</td>
<td>-0.0019</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>A'4</td>
<td>0.0150</td>
<td>0.0009</td>
<td>-0.0075</td>
<td>-0.0001</td>
<td>0.0108</td>
<td>0.0024</td>
<td></td>
</tr>
<tr>
<td>B'4</td>
<td>-0.0150</td>
<td>0.0228</td>
<td>-0.0074</td>
<td>-0.0001</td>
<td>0.0040</td>
<td>0.0038</td>
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</tr>
<tr>
<td>B4</td>
<td>-0.0436</td>
<td>0.0234</td>
<td>0.0155</td>
<td>-0.0002</td>
<td>-0.0081</td>
<td>-0.0032</td>
<td></td>
</tr>
<tr>
<td>NO Ave</td>
<td>0.0293</td>
<td>0.0270</td>
<td>0.0115</td>
<td>0.0002</td>
<td>0.0237</td>
<td>0.0024</td>
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<tr>
<td>A6</td>
<td>0.0219</td>
<td>-0.0269</td>
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<tr>
<td>A'6</td>
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<td>0.0003</td>
<td>-0.0028</td>
<td>-0.0000</td>
<td>0.0024</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>B'6</td>
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<td>0.0083</td>
<td>-0.0028</td>
<td>-0.0000</td>
<td>0.0008</td>
<td>0.0002</td>
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<td>0.0050</td>
<td>-0.0000</td>
<td>-0.0040</td>
<td>-0.0007</td>
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</tr>
<tr>
<td>Ave</td>
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<td>0.0123</td>
<td>0.0039</td>
<td>0.0000</td>
<td>0.0018</td>
<td>0.0002</td>
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</tr>
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<td>-0.1345</td>
<td>-0.0038</td>
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<td>-0.0157</td>
<td>0.0053</td>
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</tr>
<tr>
<td>A'4</td>
<td>0.0396</td>
<td>-0.0243</td>
<td>0.0019</td>
<td>-0.0001</td>
<td>0.0182</td>
<td>0.0011</td>
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</tr>
<tr>
<td>B'4</td>
<td>-0.0396</td>
<td>0.0389</td>
<td>0.0007</td>
<td>0.0001</td>
<td>0.0066</td>
<td>0.0065</td>
<td></td>
</tr>
<tr>
<td>B4</td>
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<td>-0.0002</td>
<td>-0.0129</td>
<td>-0.0057</td>
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<tr>
<td>CO Ave</td>
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<td>0.0773</td>
<td>0.0020</td>
<td>0.0002</td>
<td>0.0134</td>
<td>0.0047</td>
<td></td>
</tr>
<tr>
<td>A6</td>
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<td>-0.0633</td>
<td>-0.0011</td>
<td>-0.0001</td>
<td>-0.0045</td>
<td>0.0010</td>
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<tr>
<td>A'6</td>
<td>0.0130</td>
<td>-0.0088</td>
<td>0.0006</td>
<td>-0.0000</td>
<td>0.0045</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td>B'6</td>
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<td>0.0140</td>
<td>0.0004</td>
<td>0.0000</td>
<td>0.0022</td>
<td>0.0007</td>
<td></td>
</tr>
<tr>
<td>B6</td>
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<td>0.0552</td>
<td>-0.0006</td>
<td>-0.0001</td>
<td>-0.0057</td>
<td>-0.0008</td>
<td></td>
</tr>
<tr>
<td>Ave</td>
<td>0.0340</td>
<td>0.0353</td>
<td>0.0007</td>
<td>0.0001</td>
<td>0.0042</td>
<td>0.0007</td>
<td></td>
</tr>
</tbody>
</table>

$^a$See Figure 5.5, page 130, for the key to the location of these points.
$^b$\(\Delta \phi = \phi_{\text{exact}} - \phi_{\text{approx}}\)
$^c$Averages of the absolute values of the quantities are calculated.
potential at each of the points as well as the error function, 
\( \Delta \phi \), the difference between \( \phi_{\text{exact}} \) and \( \phi_{\text{approx}} \).

**Figure 5.5 Location of Points**

![Diagram showing points A, A', B, B', B', B', A']

Each point is denoted by a letter, indicating the nearest center, and a number, indicating its distance (in au) from that center.

It is seen from the data in Table 5.2 that \( \phi_0 \) and \( \phi_1 \), the monopole and dipole terms respectively, are generally the two dominant contributors to the approximate potential surface. The octupole term, \( \phi_3 \), which is the last term considered in the expansion contributes, on average, 0.0001 au (\( \approx \)0.06 kcal/mole) or less than 1% to the potential field in a region 4 to 6 au from the molecule. Terminating the expansion at (but including) the octupole term generates an approximate potential surface which is generally within 0.6 kcal/mole of the true surface; an average error of less than 3%.

Of particular interest is the general form of the error function \( \Delta \phi = \phi_{\text{exact}} - \phi_{\text{approx}} \). As seen from Table 5.2 the value of \( \Delta \phi \) is consistently less than zero along the internuclear axis at the electronegative end (points B4 and B6) of
the molecules. In this region, therefore, the approximate surface lies above the true surface. At points off the axis (points B'4 and B'6) \( \Delta \phi \) is positive, which indicates that the approximate surface lies below the true surface. It is this behaviour in \( \Delta \phi \) which gives rise to the apparent double minimum in \( \phi_{\text{approx}} \) referred to earlier. Note that in most cases the effect of the octupole term, the last term considered, acts to correct for this error.

Use of the expansion formula together with fragment moments which relate directly to localized distributions of charge enables one to understand features of the electrostatic potential surface in terms of local properties of the molecular charge distribution. The ionic LiF molecule, for example, is characterized by a charge transfer of nearly one electron and fragments whose charge distributions are highly spherical in nature. The breakdown of \( \phi(r) \) for LiF in Table 5.2 is typical of such an ionic distribution of charge. The charge transfer term, \( \phi_0 \), is by far the dominant term in the expansion. As a result, the corresponding potential field is predominantly dipolar in character. (The potential map for LiH in Figure 5.4 is representative of that for an ionic molecule.)

Contrast the above description of the ionic molecules to that of the polar CO molecule. In CO, there is an even greater transfer of charge than in LiF (Table 4.1); however, the fragment charge distributions in CO are polarized to a much greater extent than those in the ionic LiF molecule and, consequently,
give rise to significantly larger fragment dipole moments. Thus, in the potential expansion for CO, the contribution from \( \phi_0 \), although larger in magnitude to the corresponding quantity for LiF, is not the dominant term in the expansion. For the polar CO molecule the dipole term plays an equally important role as the monopole term in shaping the potential surface. The effect of the dipole contribution in influencing the shape of the potential surface surrounding CO is seen by comparing the potential maps in Figure 5.4 of CO and LiH (whose potential surface is dominated by \( \phi_0 \)). The charge polarizations in both the (C) and (O) fragments are directed opposite to that of charge transfer with the result that the field of \( \phi_1 \) is dipolar and of opposite polarity to the dipolar field of \( \phi_0 \). An important consequence of the oppositely directed fields of the monopole and dipole terms is the reduction in the depth of the potential well near oxygen from the value it would have based on charge transfer alone. That is, the potential well created by the large net negative charge of (O) is greatly reduced by the positive field generated by the inward polarization of charge within this same fragment.

The utility of the multipole moment expansion method is not confined to diatomic molecules. Electrostatic potential maps for the H$_2$O and the H$_2$CO molecules have also been calculated by this method of approximation. These maps, one for each of two symmetry planes in both molecules, are reproduced in Figure 5.6. The maps in this figure compare well with the
Figure 5.6

Plots showing the electrostatic potential, $\phi(r)$, derived by the multipole moment expansion method for $H_2O$ and $H_2CO$ in each of their two symmetry planes. 

Plot A: $H_2O$  
$\phi(r)$ -- $\sigma_y(xz)$

Plot B: $H_2O$  
$\phi(r)$ -- $\sigma_y(yz)$

Plot C: $H_2O$  
$\phi(r)$ -- $\sigma_y(xz)$

Plot D: $H_2O$  
$\phi(r)$ -- $\sigma_y(yz)$

$^a$For contour values see caption for Figure 5.3.
exact maps for $\text{H}_2\text{O}^{(72)}$ and $\text{H}_2\text{CO}^{(82)}$ reported by Scrocco, A. Pullman and co-workers.

The $\text{H}_2\text{CO}$ molecule is readily protonated; yet CO has never been protonated. This contrasting chemical behaviour can be understood in terms of the fragment contributions to the potential fields generated by these two molecules. From a comparison of their potential maps it is seen that the region of negative potential to which a proton is attracted is much deeper in $\text{H}_2\text{CO}$ than in CO. (The depth of the potential well in $\text{H}_2\text{CO}$ is approximately 48 kcal/mole$^{(82)}$, while in CO the potential minimum near oxygen is estimated to be $\sim$13 kcal/mole.)

The diffuse valence charge density which is present in the C fragment of CO and which is responsible for this fragment's large positive dipole moment is, in the $\text{H}_2\text{CO}$ molecule, localized into the C-H binding regions. This increased charge localization in (C) of $\text{H}_2\text{CO}$, greatly reduces the dipole moment of the fragment and, in fact, results in a reversal in the direction of polarization (the value of $\mu$(C) changes from +1.701 au in CO to -0.270 au in $\text{H}_2\text{CO}$). The decreased polarizations in (C) cause, in turn, a relaxation of the charge polarizations in the O fragment of $\text{H}_2\text{CO}$ ($\mu$(O) is reduced to 0.638 au in $\text{H}_2\text{CO}$ from its value of 1.062 au in CO).

Recall that in the CO molecule the depth of the potential well near oxygen and created by the transfer of charge to (O) is weakened by a positive field generated by a polarization of charge within (O) in a direction counter to that of charge
transfer. In \( H_2CO \), just as in \( CO \), there is a large transfer of charge from \( C \) to \( O \) (for \( H_2CO \), \( \bar{\sigma}(O) = -1.22 \) e\(^-\) and \( \bar{\sigma}(C) = +1.22 \) e\(^-\) ) which gives rise to a strong dipolar field. However, in \( H_2CO \) the charge polarizations within the \( O \) fragment, while still present, are reduced in magnitude. Correspondingly, the depth of the potential well near oxygen is deeper in \( H_2CO \) than in \( CO \).

In summary, the usefulness of fragment moments to predict the form of \( \phi(r) \) goes beyond providing a rapid and accurate method for its evaluation. The nature of a system's electrostatic potential map is readily understood and qualitatively predictable in terms of the fragment multipole moments.
CHAPTER 6

SUMMARY AND CONCLUSIONS

A molecular system may be uniquely partitioned into well defined quantum mechanical subregions of total space. Each subregion—termed a virial fragment—possesses properties analogous to those of the total isolated molecule: the fragment kinetic and potential energies are related by the virial theorem,

$$2T(\Omega) = -U(\Omega)$$

and, for a molecular system in a state of equilibrium, a fragment total energy, $\bar{E}(\Omega)$, obeys the further virial relationship

$$\bar{E}(\Omega) = -\bar{T}(\Omega).$$

A necessary condition of the partitioning theory is the zero-flux requirement imposed on the surfaces bounding the virial fragments. Such surfaces define the fragment in a natural and unambiguous manner in terms of a property of the experimentally observable charge distribution of a system—whether it be an isolated molecule, a collection of molecules or a crystal. The zero-flux surface condition allows any $N$-nuclear centered molecular system to be maximally partitioned into $N$ quantum subspaces, each containing a single nucleus. Thus, a result of the virial partitioning procedure is the division of a molecule into a collection of single-center or atomic-like fragments.
The physical significance of the virial Partitioning Theory is based upon the observation that the extent to which the properties of a fragment are retained in different molecular systems is determined by the extent to which the charge distribution of the fragment remains unchanged in those systems. Since a virial fragment is defined in terms of spatial features of the molecular charge distribution, the partitioning theory naturally accounts for any constancy of properties associated with the fragment in those chemical environments where the fragment charge distribution exhibits only small differences. As a consequence of the zero-flux surface condition the changes in a charge distribution which occur with fragment transfer are minimized within the domain of the virial fragment, that is, for any other surface one either misses part of the fragment which changes little or else one includes part of the neighbouring fragment which may change a great deal. Thus the Virial Partitioning Theory yields chemically identifiable fragments by maximizing the retention of fragment properties in different molecular systems.

In those fragments which exhibit large changes in properties in various chemical systems, (as does the hydrogen fragment in the AH series of molecules), there are correspondingly large changes in the charge distributions of these fragments. Further, the changes which are incurred generally parallel one's chemical intuition and notions based on concepts such as electronegativity.
Calculated numerical values of virial fragment properties (particularly populations), because of their direct relationship to the charge distribution, are physically meaningful and understandable in terms of the observed distribution of charge. For example, the charge density maps of the cyano containing molecules (Figures 2.3 and 2.4) depict the cyano carbon as a thin saucer-shaped fragment, and, consequently, reflect this fragment's highly depleted population (Table 2.7). The significant differences often encountered between virial fragment populations and those computed from the orbital based partitioning schemes are due, in part, to the fact that, unlike virial populations, orbital based populations do not refer to any well-defined regions of real space, but instead, are arbitrarily defined in terms of a many-dimensional mathematical function.

For continuous changes in a molecular charge distribution, there are corresponding continuous changes in the partitioning surfaces and the fragments they define. Thus, Virial Partitioning Theory may be applied to the study of dynamical changes such as those occurring in chemical reactions. Since each fragment of a system obeys the virial relationship during the entire course of a chemical reaction, the virial theorem may be applied to the energy changes experienced by each of the fragments:

$$-2\Delta \overline{T}(\Omega) = \Delta \overline{U}(\Omega)$$

If the changes in energy correspond to two states in
equilibrium, the total fragment energy is related by
\[ \Delta \tilde{E}(\Omega) = -\Delta \tilde{T}(\Omega) \]
Thus one can monitor the relative stability of a fragment in terms of the changes in the potential interaction energies during the course of a reaction.

Specific application of the Virial Partitioning Theory to the gas phase nucleophilic substitution reactions of
\[ F^- + CH_3F \rightarrow [F-CH_3-F] \rightarrow CH_3F + F^- \]
and \[ CN^- + CH_3F \rightarrow [CN-CH_3-F] \rightarrow CH_3CN + F^- \]
shows that during the initial stage of the reaction (attack of the nucleophile and subsequent formation of the transition state) (1) both nucleophilic species increase in stability at the transition state relative to that of the corresponding negative ions, (2) both leaving groups (the F fragment in each case) decrease in stability at the transition state relative to that in the reactant CH₃F molecule and (3) the CH₃ fragment becomes more stable in the transition state. These results indicate, therefore, that the only factor contributing to the increased energy of the transition state in both reactions is the destabilization of the leaving fluorine fragment; all other fragments act to lower the total energy along the reaction path (Table 3.2). The larger activation energy for the CN⁻ + CH₃F reaction \( (\Delta E^+ = 22.6 \text{ kcal/mole} \) compared with 7.26 kcal/mole for the F⁻ + CH₃F reaction) is due to the greater extent to which the leaving F fragment has separated from the substrate and has become more
destabilized at the \([\text{FCH}_3\text{CN}]^-\) transition state relative to that in \([\text{FCH}_3\text{F}]^-\).

The ability of Virial Partitioning to monitor changes in the total energy in a reaction sequence not only allows one to follow fragment stability but also makes it possible for one to isolate those spatial regions or fragments of a reacting system which are commonly referred to as "energy rich" regions (energy rich in the sense that they harbour their instability in the form of an increased potential energy). Such is the case in the nucleophilic reactions where the \(\text{H}\) fragments, because of "crowding" by adjacent fragments, each become destabilized by \(\sim 15\) kcal/mole at the transition state. This stored "compression energy" is released as the systems proceed to products and, thereby, serves as a driving force for further motion along the reaction coordinates. Thus, the concepts of "high energy" bonds and "energy rich" regions and the role they play in biochemical reaction mechanisms may be quantitatively probed with the Virial Partitioning Theory.

Molecular geometry is a further area of study which may be pursued at a fundamental level by the procedure of Virial Partitioning. Changes in the structural framework of a molecule can be related directly to molecular stability via the virial theorem and in terms of localized energy changes within the virial fragments. The energy changes can, in turn, be analysed with respect to observable changes in the molecular charge distribution.
The results of the method when applied to the geometry of hydride molecules of the type $AH_n$ distinguish between those molecules possessing non-bonded valence electrons ($NH_3$ and $H_2O$) and those which do not ($BH_3$ and $BeH_2$). For the former molecules, the increase in stability, which occurs on bending the molecules from their respective planar and linear structures to their corresponding pyramidal and bent structures, is due in part, to (1) a transfer of electronic charge density from the central fragment (from $O$ or $N$) to the $H$ fragments which causes a lowering of the electron–electron repulsion energy within this central fragment, and (2) a transfer of charge density from the non-binding to the binding region of the central fragments. (Fig. 4.2) thereby minimizing the destabilizing effect of decreased electron-nuclear attraction caused by the charge transfer out of the central fragment (Tables 4.2 and 4.3).

The $BeH_2$ and $BH_3$ molecules are most stable as linear and planar molecules, respectively. Any change in the bending mode away from these stable geometries causes (1) a transfer of charge from the $H$ fragments into the central fragment—a redistribution of charge which decreases the electron-nuclear attractions within the $H$ fragments, and (2) an accumulation of charge into the non-binding region of the central fragment (Fig. 4.2) which reduces further the average electron-nuclear attractions within the molecules.

The inherent instability of the $C_{2v}$ and $C_{3v}$ geometries
of BeH$_2$ and BH$_3$, respectively, is built into their static charge distributions as an outward curvature of their A-H bond paths (the ridge of maximum charge density linking neighbouring nuclei). The curving out of bond paths reflects the destabilizing outward shift of charge density (to non-binding regions) referred to above. Correspondingly, the inward curvature of the bond paths in both the C$_2$v and C$_3$v forms of H$_2$O and NH$_3$, respectively, indicate the inherent stability of these structures.

Electrostatic potential maps are becoming increasingly useful as an interpretive chemical tool. Since exact calculations of potential surfaces require, in general, large amounts of computer time, accurate approximate methods for their generation becomes a necessity. Using the formulation of the multipole-moment expansion approximation in conjunction with the moments of virial fragments, such an alternate method is achieved. The electrostatic potential surfaces, generated by this method of approximation, approach the exact surface to within an average error of less than 3% (or to within ~0.6 kcal/mol of the exact surface). These results are based on a truncation of the series expansion at (but including) the octupole term (Table 5.2).

In addition to their relatively fast convergent properties in the multipole moment expansion, virial fragment moments possess other inherent advantages. Virial fragments are unambiguously defined; they are physically meaningful in that
they relate directly to the charge density localized in a well-defined region of real space, and, because they relate to localized charge density, they allow characterization of the electrostatic potential surface terms of the charge distribution and properties of the component functional groups of a molecule.

A natural extension of the approximation method is the generation of electrostatic potential surfaces of large molecules using a collection of fragment moments obtained from smaller molecules. Such a proposal is based on the fact that the Virial Partitioning Theory naturally accounts for the transferability of fragment properties among molecular systems. Hence, from a judicious choice of a number of small molecules, one can obtain a compilation of fragment moments from which the potential fields of large molecular systems could be generated quickly and without the use of wavefunctions.

In conclusion, one observes that if a molecular system is partitioned into fragments by surfaces which satisfy the zero-flux condition, then the chemistry of the total system is faithfully reflected in the properties of the individual fragments. Virial Partitioning Theory thus parallels the operational structure of descriptive chemistry where the properties of the total system are qualitatively predicted, catalogued and interpreted in terms the properties of its atomic or functional group constituents and the interactions between them. The working model of chemistry which has
evolved as a result of observations of chemical phenomena has a theoretical basis—in the properties of the virial fragments as defined and predicted by quantum mechanics.
APPENDIX A1

LOGE THEORY

The loge theory of Daudel and co-workers\(^{(22,23)}\) represents an alternate method of molecular partitioning. These authors have reasoned that there should be some "best" decomposition of the physical space of a system into a number of mutually exclusive regions called loges. The "best" loges represent the most probable division of the physical space into localized groups of electrons.

Consider the partitioning of a total system containing \(N\) electrons into two mutually exclusive loges \(\Omega\) and \(\Omega'\). Then, the probability of the event that \(n\) electrons will be found in the loge \(\Omega\) when the remaining \((N-n)\) electrons are confined to \(\Omega'\) is

\[
P_n (\Omega) = \frac{N!}{n!(N-n)!} \int_{\Omega} \cdots \int_{\Omega} dr_1 \cdots dr_{N-n} \int_{\Omega'} dr_{N-n+1} \cdots \int_{\Omega'} dr_N \Gamma^{(N)}(r_1, r_2, \ldots, r_N) \tag{Al-1}
\]

where \(\Gamma^{(N)}\) is a diagonal element of the spinless \(N\)-particle density matrix,

\[
\Gamma^{(N)}(\xi_1, \xi_2, \ldots, \xi_N) = \Gamma \psi^*(\xi_1, \xi_2, \ldots, \xi_N) \psi(\xi_1, \xi_2, \ldots, \xi_N)
\]

and the primes denote products of space and spin variables, \(\Gamma' = \Gamma \sigma_1\). The binomial coefficients in equation (Al-1) account for the indistinguishability of the electrons, so that it does not matter which \(n\) electrons are considered to be in \(\Omega\) when the remaining \((N-n)\) electrons are in \(\Omega'\). Since the wave-
function is assumed to be normalized, one has

$$\sum_{n} P_n(\Omega) = 1$$  \hspace{1cm} (A1-2)

The average number of particles in $\Omega$ is

$$\bar{N}(\Omega) = \sum_{n} n P_n(\Omega) = \int_{\Omega} \rho(x) \, dx$$  \hspace{1cm} (A1-3)

If a single event has a dominant probability, it is referred to as the leading event. If $P_n(\Omega)$ is a leading event and the probability distribution of the other events is symmetrical about $P_n(\Omega)$, in particular, if the probabilities of the "satellite" events $P_{n-1}(\Omega)$ and $P_{n+1}(\Omega)$ are equal to one another, then $\bar{N}(\Omega)$ will equal $n$. One must distinguish between the number of electrons localized in a given loge to yield a leading event and the average occupation number of the loge.

Aslangul\(^{(24)}\) has proposed that the concepts of information theory be used to define the "best" division of a system into loges. According to this theory,\(^{(81)}\) one's knowledge about a system is a maximum when the "missing information function", $I(P_n, \Omega)$ is minimized, where

$$I(P_n, \Omega) = -\sum_{n} P_n(\Omega) \ln P_n(\Omega)$$  \hspace{1cm} (A1-4)

If the probability of one particular event ($n$ particles in $\Omega$) approaches a certainty, then

$$P_n(\Omega) \rightarrow 1 \hspace{1cm} \text{and} \hspace{1cm} \sum_{m \neq n} P_m(\Omega) \rightarrow 0$$
In this case, one's knowledge of the system would be maximal as it would be known with certainty that \( n \) electrons are in \( \bar{\Omega} \) and \( (N-n) \) electrons in \( \bar{\Omega}' \). Correspondingly, in this case, \( I(P_n, \bar{\Omega}) \) would approach zero. At the other extreme, when all events are equally probable, one's knowledge of a specific state would be minimal and the missing information function would be maximized.

The underlying assumption of loge theory is that there are spatially localized groupings of electrons and, in particular, that these groupings correspond to pairs of electrons confined to regions of space identifiable as core regions, bonded pair regions and lone pair regions. Investigations of actual molecular charge distributions\(^{(68,83)}\) has shown that this assumed model is, in general, incorrect. In systems where the nuclear charge is less than \( \sim 20 \) a core region can be defined and, in certain simple molecular systems in which the localization of the charge density is well defined by "deep minima" (for example, in LiH, BeH\(_2\), and BH\(_3\)) bonded electron pair regions can be defined. In general, however, the minima in the charge density of a molecule are not so well defined and, consequently, one does not find localized bonded or non-bonded pairs of electrons. One does find localized atomic distributions. These are "atoms" in molecules.
APPENDIX A2

CONVERSION TABLE FROM ATOMIC UNITS

1 \text{ au} = \text{ a}_o = 0.52917 \times 10^{-8} \text{ cm} \quad \text{(length)}

= \frac{e^2}{a_o} = 4.3592 \times 10^{-11} \text{ erg} \quad \text{(energy)}

= \frac{e^2}{a_o^2} = 8.2377 \times 10^{-3} \text{ dyne} \quad \text{(force)}

= ea_o = 2.5415 \text{ Debye} \quad \text{(dipole moment)}

a_o = \frac{\mu^2}{m_e e^2}
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