ORBITAL MODELS AND THE ELECTRON DISTRIBUTION:

APPLICATIONS AND EXTENSIONS OF THE THEORY OF ATOMS IN MOLECULES

By

© THOMAS STEPHEN SLEE, B.Sc.

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AUTHOR: Thomas Stephen Slee, B.Sc. (University of Sussex)

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ABSTRACT

This thesis explores the relationship between the recently developed theory of atoms in molecules and the simple orbital models of electronic structure which form the basis of current chemical thinking. In so doing it provides a new viewpoint from which to study many essential chemical concepts: concepts originating from qualitative orbital models.

The formal aspects of the theory of atoms in molecules are reviewed. Developed in the laboratory of Professor Bader, this theory provides a quantum mechanical definition of an atom in a molecule and its properties. It also exploits the observed topology of the electron density to define molecular structure and its change.

The relationship between qualitative orbital models and atomic and bond critical properties is analysed, first qualitatively and then quantitatively. The analysis starts with a study of atomic properties and the properties of bond critical points in diatomic hydrides and some simple organic molecules. A theoretical framework is then developed within which chemical effects on molecular electron distributions can be studied and interpreted.

This framework is used in a study of substituent effects on the ethyl, vinyl and carbonyl groups, and then applied to two other problems – the interpretation of protonation energies of carbonyl compounds and an investigation of the concept of homoaromaticity.

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I dedicate this thesis to my Mother and to the memory of my Father. I wish nothing more than that he could be here to see it finished.

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INTRODUCTION

Quantum chemistry is an interdisciplinary subject in the fullest sense of the word: it is not simply a branch of physics and neither is it just a branch of chemistry. To justify this contention and to appreciate its consequences, of which much more below, it is appropriate to take a glance at the history of the theory of valence (Russell 1971).

The roots of modern chemical theory lie in the experiments and interpretations of Lavoisier, Proust, Priestley and others in the late eighteenth century, which culminated in Dalton's law of multiple proportions. Berzelius stated this law in the words "In a simple series of compounds made up of the same elements, a simple ratio exists between the weights of one and the fixed weight of the other element." (Jaffe 1976, p.87) Dalton took a daring step further and suggested that this law could be explained by postulating that each chemical element consisted of one kind only of atoms, all alike, and that the atoms of different elements could be distinguished by their characteristic weight.

The nineteenth century saw the slow development of a theory of valence which was based entirely on chemical experiment, which is to say the study of chemical reactions. Physics had some indirect influence on the development of valence theory through the essential role of electrochemistry, but until the twentieth century none of chemistry was understood in terms of a physical theory: the mechanisms holding Dalton's (assumed particulate) atoms together were assigned some electrical origin, but defied any further insight into their origin and nature. The notion of a chemical bond was developed by Kekule, Frankland, Butlerov and others in order to account for and organise chemical behaviour, but there was no physical understanding underlying the concept. As Frankland said when he introduced the name "bond"

> "It is scarcely necessary to remark that by this term [bond] I do not intend to convey the idea of any material connection between the elements of a compound, the bonds actually holding the atoms of a chemical compound being, as regards their nature, entirely unknown". (quoted in Russell 1971, p.90)

Chemical atoms and bonds were thus primary concepts in the sense that they were unobservable and that their nature or structure was unknown. This did nothing to diminish their importance, however, for they served as the central concepts around which the growing number and variety of chemical reaction were organised, classified and thus partially understood.

The early twentieth century saw the encroachment of physics into valence theory with the beginnings of an understanding of the electronic structure of atoms. The implications of the discovery of electrons and atomic nuclei were different for chemistry and physics, however, with chemical theory developing along different lines from physical theory. The distinction is apparent in the chemical emphasis of Lewis' model of the atom and of the covalent bond, which encompassed a great many chemical phenomena and yet which had only a tenuous relation to a physical theory of the atom.

The development of quantum mechanics helped to bring the two types of theory closer together, and the Schrödinger equation has often been claimed as the basis for the understanding of chemistry (most famously by Dirac), a statement that even Lewis accepted. Valence theory became quantum chemistry. In recent decades methods have been developed which allow accurate computer solutions of the Schrödinger equation (Schaefer 1985) and the impact of these methods has been such that quantum chemistry is often treated as synonymous with the search for more accurate solutions to Schrödinger's equation for molecular systems — with ab initio electronic structure theory. If this was the case, quantum chemistry would indeed be simply a branch of physics: but it is not the case and the problems of understanding chemistry cannot be reduced simply to numerical solutions of Schrodinger's equation.

What aspects of valence theory fall outside the realm of ab initio electronic structure theory? From one perspective it could be claimed that most do. To pick up any organic or inorganic chemistry textbook is to appreciate that one of the principal problems of chemical theory is to find ways of tying together the massive amount of data that make up modern chemistry into a coherent body of knowledge — to relate the structures and reactions of chemical compounds to each other in a consistent manner. Further, it becomes immediately apparent that the empirical chemical notions of atoms and bonds are absolutely essential to this central task of chemical theory, and that ab initio electronic structure theory per se has little to say about the problem. A computer calculation on a molecule produces an energy, a wavefunction and nowadays also possibly spectroscopic properties of the molecule. This is not equivalent to understanding, in the sense that we cannot (using ab initio electronic structure theory alone) say how the molecule will react with nucleophiles or electrophiles, we cannot suggest how easily the molecule will dissociate, and we certainly cannot know how the replacement of a CH group by a nitrogen atom (for instance) will alter the chemical behaviour of the molecule. In short, although electronic structure theory can tell us about the properties of an isolated molecule or process, it does not provide any means of relating one molecule's behaviour to that of another. Any theory which claims to yield an understanding of chemistry must make some comment on this central problem. Electronic structure theory cannot be synonymous with quantum chemistry if the word "chemistry" is taken seriously.

In order to tackle the problem of understanding molecular behaviour in the chemical sense just described, a series of qualitative models of electronic structure have been developed from quantum mechanics, maintaining much of Lewis' emphasis and concepts. First came resonance theory (although some aspects of resonance theory were developed from chemical experiment alone, with no reference to quantum mechanics, by Arndt (Russell 1971)) and then a variety of approaches based on molecular orbital theory using the linear combination of atomic orbitals (LCAO) approximation, and particularly on Hückel theory. Chemical concepts such as atomic charge, bond order, conjugation and electronegativity, were taken from their purely empirical background and related to elements of simple orbital theories by Mulliken, Coulson and others. In this way, theoretical chemistry became a combination of empiricism and simple semi-empirical orbital models. It remains that way today.

The problem of taking chemical concepts and relating them to the wavefunctions produced by today's computers has only recently begun to be solved, and it is this problem that is tackled in this thesis. One of the motivations for the mapping of chemical concepts onto elements of ab initio electronic structure theory is to enable more reliable and more accurate predictions to be made of the properties of related molecules from a given calculation, and to enable some prediction of the molecule's reactivity to be made from the single point calculations which are the staple of computational molecular quantum mechanics. This is what is meant by an "understanding" of a molecule's electronic structure — the calculation become more than simply a hugely complicated wavefunction and an energy. It can be related to other calculations and to chemical experiment: in short, it can take its place as a part of chemistry.

Chapter 1 serves to review the current state of the theory of atoms in molecules, a theory which has solved the problem of relating the fundamental chemical concepts of atoms, bonds and molecular structure to electronic structure theory and to chemical experiment within a quantum mechanical framework. The theory shows that atoms and bonds can be defined in terms of topological features of the molecular electron distribution. Chapter 2 is primarily concerned with relating other chemical concepts, those currently based on simple orbital theories, to the electron distribution and to the properties of the atoms and bonds of Chapter 1. It further develops the framework within which chemical problems can be discussed from ab initio calculations, and in Chapters 3 and 4 some applications of the theory are presented.

CHAPTER 1

THE ANALYSIS AND CALCULATION OF MOLECULAR CHARGE DISTRIBUTIONS

This chapter serves to introduce the theory of atoms in molecules and to critically assess its current status, with an attempt to keep in mind the basic problem I wish to tackle: how to better apply the theory of atoms in molecules to problems of interest to chemists. The chapter acts as a background for the original work of this thesis by summarising previous relevant work, as well as trying to assess its scope and limitations.

Section 1.1 describes the empirical basis of the theory by showing how the qualitative form, or topology, of molecular charge distributions can be properly described and analysed. This description is carried out in terms of the gradient vector field of the charge distribution, and in particular the number, kind and connectivity of its critical points. The analysis leads to a topological definition of the structural elements that make up molecules: atoms and bonds. Section 1.1 also discusses how the Laplacian of the electron distribution brings out the fine structure that cannot be so easily seen in the density itself. In particular, the manner in which topological features of the Laplacian mimic concepts of simple models of electronic structure, such as shell structure and lone pairs, is discussed.

Prompted by the identification of atoms in molecules with particular bounded regions of space, Section 1.2 asks whether such regions can have quantum mechanical significance. The investigation of this question provides the theoretical basis for the definition of atoms in molecules, and involves a generalisation of the variational principle to bounded regions of three dimensional position space. In classical mechanics the action principle can be made to yield not only equations of motion for dynamical systems but also conservation laws and definitions of mechanical properties of systems, by removing the constraint that variations in the dynamical variables have to vanish at the time end points. Analogously, in defining quantum mechanical properties for bounded regions of space a variational constraint is removed, but for stationary states it is removed from the space boundaries rather than the time boundaries of the system. It is found that the variational principle can be unambiguously generalised in this manner only to particular regions of space, and that the set of such regions contains the topologically defined atoms in molecules. Section 1.2 also discusses the regional forms of special theorems satisfied by optimal wavefunctions: the hypervirial theorem, the Hellmann-Feynman theorem, the Ehrenfest theorem and the virial theorem. Lastly, the definition of atomic properties is considered, with an emphasis on the energy of an atom in a molecule.

The formalism developed in Sections 1.1 and 1.2 relies on the availability of accurate molecular charge distributions both to justify its underlying assumptions and to be applied to particular problems of interest. At the moment such distributions are best obtained by ab initio computation, though experimental densities are becoming of acceptable quality. Section 1.3 discusses the accuracy of the theoretical models used in the calculation of molecular electron distributions. Almost all the electron distributions analysed to date in terms of the theory of atoms in molecules have been obtained from single determinant wavefunctions constructed from a basis set of atomic orbitals, and calculated by the Roothaan-Hartree-Fock self-consistent field procedure, so it is essential to know the extent to which such distributions can be trusted. In particular, it is only in the last twenty or so years that calculations of sufficient accuracy have become available to justify with reasonable confidence the assumptions of the theory concerning the qualitative form adopted by ground state electron distributions. A discussion of the basis set dependence of calculated properties of atoms in molecules is given, completing the chapter.

1.1 THE TOPOLOGY OF MOLECULAR CHARGE DISTRIBUTIONS

There are only a few theorems concerning the general form of the electron distribution in molecules (Smith 1982, Bader et al. 1981). The Kato electronuclear cusp condition (1957) states that the exact charge density exhibits a cusp at positions of the nuclei, as does the exact Hartree-Fock (HF) density. An upper bound has been given for the electron density at the nucleus of an atom by Hoffmann-Ostenhof et al (1978) in terms of the nuclear charge. At the other extreme of distance, the asymptotic exact density falls off exponentially with distance from the nuclei (Ahlrichs 1972). Apart from these "limiting case" theorems, which apply to situations where the interelectron potential is unimportant, our knowledge of the qualitative features of molecular electron distributions is based entirely on the observation of calculated or experimentally determined distributions.

Experimental distributions from x-ray crystallography are currently less accurate than those calculated directly from quantum mechanics for small and medium-sized molecules. Realistic theoretical densities have only been available for study since the development of computer programs for the calculation of the electronic structure of molecules, so it is only in the last twenty years or so that soundly-based claims concerning the forms of electron distributions have been possible. Section 1.3 deals with the approximations that have to be made in computations of molecular electronic structure and properties. In this section it is assumed that calculated densities do describe the main features of exact distributions correctly, and some observations that have been made concerning qualitative features common to most or all molecular charge densities are presented. I will show how these observations can be used as a basis for a description of the <u>structure</u> of molecules (Bader et al 1979a, 1981). An extension of this description to encompass the concept of structural change and <u>structural stability</u> has also been achieved (Bader et al 1979b, 1981). Its direct relevance to this thesis is limited, as structural changes only appear briefly, in Chapter 4, and a discussion of structural change in molecules is thus postponed to that chapter. A topological analysis of the Laplacian of the electron distribution has been shown to yield chemically interesting results (Bader and Essen 1984, Bader et al 1984), and is discussed at the end of this section.

The electron distribution is a scalar field defined in a three dimensional space. It is infinitely differentiable everywhere except at the positions of nuclei, where it has a cusp and is not differentiable.

In trying to identify and make rigorous the notions of molecular structure and structural stability it is the qualitative features of electron distributions that need to be characterised — the topology, to use the word informally — and in particular those features that are common to all ground state molecular charge densities. This characterisation is achieved by investigating the number of maxima, minima, and other stationary points that the distributions possess. The first task is thus to classify the types of stationary point that may occur in a function of three variables.

Consider a general scalar function $\rho(x)$, where $x = (x_1,x_2,x_3)$ is a coordinate in three dimensional space. A stationary point, or critical point, in such a function is defined by the condition that its first derivatives all vanish:

$$\partial\rho/\partial x_i = 0, \qquad i=1,2,3 \qquad [1.1.1]$$

The different types of critical point are classified by their second derivatives, the collection of which forms a symmetric matrix called the Hessian of ρ. The Hessian can be diagonalised to yield the three principal curvatures (the eigenvalues) and the corresponding principal axes (the eigenvectors) of ρ at the critical point. The number of non-zero principal curvatures is called the rank of the critical point. Most critical points that occur in molecular electron distributions are of rank three. (Critical points of rank less than three are called degenerate critical points or singularities. They only occur in "unstable structures" and will be discussed briefly in Chapter 4). Maxima (or 3-saddles) have three negative principal curvatures, minima (or 0-saddles) have three positive principal curvatures, and there are two intermediate types of critical points, which are called 1-saddles, which have one positive and two negative principal curvatures, and 2-saddles, which have two positive and one negative principal curvatures. If the <u>signature</u> of a critical point is defined to be the number of positive principal curvatures minus the number of negative principal curvatures, then critical points can be classified by their rank and signature, written as (rank, signature).

A more complete description of the form of a scalar field can be obtained by investigating the whole of its <u>gradient vector field</u> (Bader and Runtz 1975, Collard and Hall 1977). This can be done pictorially by plotting sets of <u>orthogonal trajectories</u> or <u>gradient paths</u> of ρ: those curves whose tangent at every point is the gradient vector of ρ, the lines of steepest ascent through the field. Each and every such path must start and finish at a critical point, or at infinity. In the terminology of the subject, the starting point is called the α-limit set, and the terminus is the ω-limit set: though in the cases that arise when ρ is the molecular electron distribution, each set comprises only one point. The ω-limit set is called the <u>attractor</u> of the path, and the α-limit set the <u>repellor</u>. The set of paths for which a critical point acts as attractor is called the <u>stable manifold</u>, or <u>basin</u>, while the set of paths for which a critical point acts as a repellor is called the <u>unstable manifold</u>. In three-dimensional fields, (3,-3) critical points (maxima) are global attractors of the field, as they form the ω-limit set for a collection of trajectories, but do not form the α-limit set of any trajectory: they have only stable manifolds. Minima are global repellors of the field, and the 1- and 2-saddle points act as attractors and repellors to different dimensional manifolds. The unstable manifold of a (3,-1) critical point is a line consisting of two gradient paths, each of which terminates (in stable structures) at a maximum. The stable manifold of such a point is a surface of gradient paths which converge on the critical point in the plane defined by its two negative principal curvatures.

This completes the classification of the structural elements that occur in (stable) scalar functions of three dimensions. The electron distribution has been observed to show some consistent characteristics throughout a large number and variety of molecules, and this allows the identification of the structural elements of such distributions with "chemical" concepts. The observations that form the basis for the description of molecular structure come from the analysis of hundreds of molecules, mainly composed of hydrogen and second row elements but with some third row elements also included, so while their status is still one of empirical extrapolations, the base for these extrapolations is large.

The following observations have been found to hold for all the ground state molecular electron distributions studied to date, with the exceptions noted:

Observation 1. The only maxima in electron distributions of molecules occur at the positions of nuclei.

The converse of this, that the electron distribution is a maximum at the position of every nucleus, holds in all the cases studied in this thesis and in the vast majority of "normal" chemical situations. Some highly electronegative atoms bonded to hydrogen, however, remove so much charge from the hydrogen atom that there is no longer a maximum at the position of the hydrogen nucleus. Examples given by Bader et al (1979a) are FH^+ and NeH^+. This disappearance of the maximum at the nucleus has not been observed for any atom with a core density.

<u>Observation 2.</u> In those molecules to which structural formulae have been uncontroversially assigned (the vast majority of organic molecules), in the neighbourhood of their equilibrium geometry, between each and every pair of nuclei that have traditionally been considered to be bonded one and only one (3,−1) critical point is found. The unstable manifold of this point forms a line connecting the two nuclei. Conversely, no (3,−1) critical point, (and no connecting unstable manifold) is observed between nuclei that have not been considered as bonded in uncontrovetsial structural formulae.

Some calculations at inadequate basis sets have shown off-nuclear maxima at positions between the nuclei, in apparent contravention of observation 1. These maxima have all disappeared as the quality of the basis set was improved. In addition, it is shown in section 1.3 that electron correlation should mitigate against the appearance of such off-nucleus maxima as a result of correlation along the bond axis, so that if observation 1 is true for HF densities it should also be true for exact densities.

There are two corollaries of these observations:

<u>Corollary 1.</u> (3,+1) critical points only occur inside a ring. The unstable manifold of the (3,+1) point forms a surface, the vertices of which are nuclei and the edges of which are unstable manifolds of (3,−1) critical points.

<u>Corollary 2.</u> Minima only occur inside a cage. The unstable

manifold of the minimum forms a volume, the bounding surfaces of which are the unstable manifolds of the (3,+1) critical points, the vertices of which are nuclei, and the edges of which are the unstable manifolds of the (3,-1) critical points.

The qualitative form of electron distributions is thus extremely simple. The lack of off-nucleus maxima is the most obvious example of this simplicity, another is that "double bonds" do not show up in the electron density as two lines linking the "bonded" nuclei as may have been suspected: instead only one line is ever seen. The observations reflect the fact that the topology of the electron distribution is governed largely by the nuclear-electron attraction, with the interelectron potential making quantitative changes, but usually not qualitative ones. In many cases, the structure of the gradient vector field of the nuclear potential is the same as that of the electron distribution for the same nuclear geometry (Tal et al 1980). Exceptions do occur, for instance in some ring and cage structures. An example is tetrahedrane at its equilibrium geometry where the cage in the electron distribution appears in the nuclear potential field as a single point — a degenerate critical point. The reason for this is simple to see. No minima can occur in the electron nuclear potential (V_{ne}), which satisfies Poisson's equation everywhere but at the nuclear positions X_c.

$$\nabla^2 V_{ne}(x) = \sum_c \delta(x-X_c) \qquad [1.1.2]$$

A minimum has three positive principal curvatures, and so must have a Laplacian greater than zero, in contravention of this equation.

The formal definitions of the elements of molecular structure can now be given. A nucleus and its basin form an <u>atom</u>. In the neighbourhood of an equilibrium geometry, two atoms are said to be bonded if their nuclei are linked by the unstable manifold of a (3,-1) critical point. This critical point is called a bond point, and its unstable manifold a bond path. In the more general situation of geometries far from equilibrium, to which the notions of chemical bonds are less applicable, the unstable manifold is called an interaction line (Bader and Essén 1984) The collection of bond paths is said to form the molecular graph of the system. The stable manifold of a bond point is called the interatomic surface, as it is a dividing surface between the two atomic basins.

A single picture is, it is said, worth a thousand words, and so examples of molecular charge densities and their topological features are shown on the following page. Figures 1.1.1 to 1.1.3 and the captions aim to flesh out the formal definitions of the above paragraph by providing examples of how electron distributions can be portrayed, and of their topological features.

The definition of elements of molecular structure shows that the most basic qualitative concepts of chemistry have analogues in the topological features of observed charge distributions, this being a result of the importance of the nuclear—electron potential in determining the qualitative aspects of such distributions. Traditionally, atoms have also been assigned properties in order to explain the behaviour of molecules in terms of their structure. The most important of these atomic properties are valencies and electronegativities, which are approximately transferable between atoms, and atomic charges, which are more dependent on the environment of the atom. What properties can be

Figure 1.1.1

Three views of the charge density in ethene, taken from Bader et al (1981). The left hand side of each figure is a relief diagram which corresponds to the contour map to its right. The values of the contours increase from the outermost one inwards in steps of 2×10^n, 4×10^n, and 8×10^n with n beginning at -3 and increasing in steps of unity. This set of contours is used throughout the thesis for maps of the electron density.

Figure (a) shows the electron density in the molecular plane of ethene. The maxima are the carbon and hydrogen nuclei.

Figure (b) shows the density through a plane perpendicular to the molecular plane, and containing the carbon nuclei: the "π" plane. Again, the carbon nuclei appear as maxima.

Figure (c) shows the density in the plane bisecting the two carbon nuclei. In this projection the molecular plane is vertical. The contours of the density in Figure (c) are thus elongated in the "π" plane, showing the greater amount of electron density in that plane.

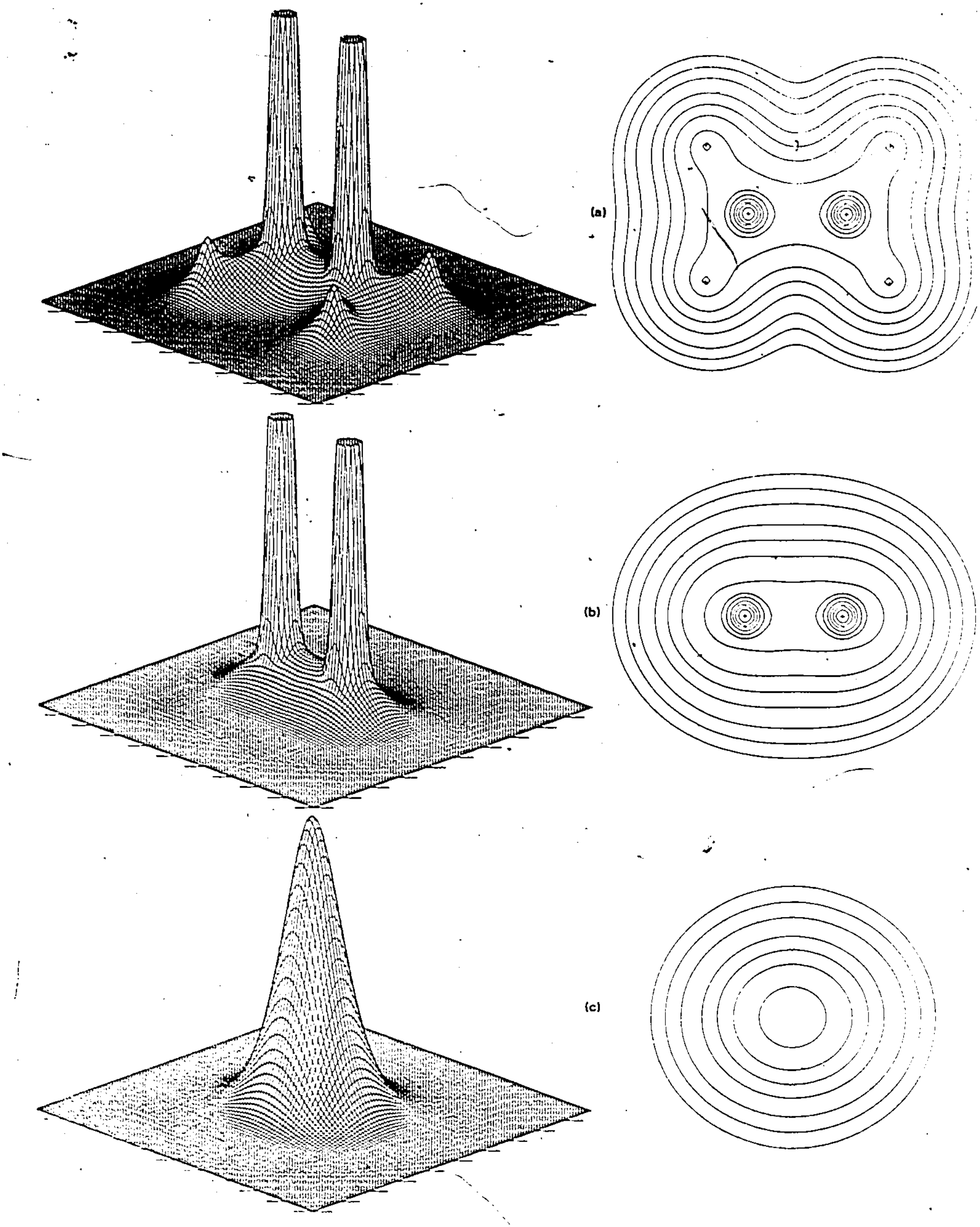

(a)
(b)
(c)

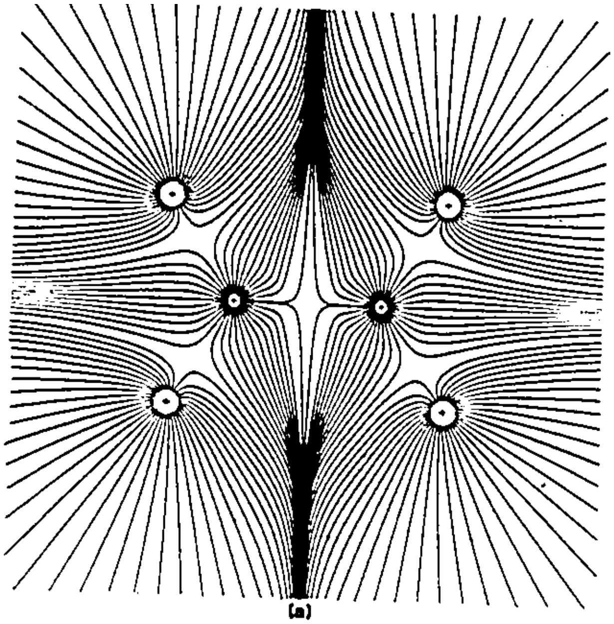
Figure 1.1.2

The gradient vector field of the electron density in the molecular plane of ethene (see Figure 1.1.1.(a)), taken from Bader et al (1981). Each line represents a trajectory of $\nabla\rho(x)$: a line of steepest ascent through the electron density.

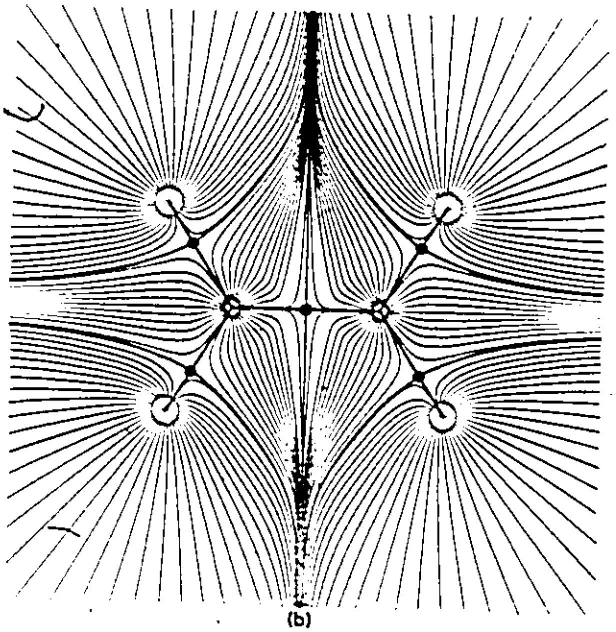
In Figure (a) only those trajectories which originate at infinity and terminate at the positions of nuclei are shown. The set of trajectories which terminate at a given nucleus (attractor) defines the basin of that attractor.

Figure (b) is the same as Figure (a) except that the trajectories which terminate and originate at (3,-1) critical points are indicated by heavy lines. The position of the (3,-1) critical point is indicated by a full circle. The pair of trajectories which terminate at each (3,-1) critical point (originating at infinity) are part of the interatomic surface it defines, and mark the boundaries of the atoms. The pair of trajectories that originate at the (3,-1) critical point (terminating at the nuclei) define, the bond paths, and together make up the molecular graph.

Figure (c) shows the interatomic surfaces and the bond paths superimposed on a contour map of the electron density of the molecular plane of ethene.



(a)



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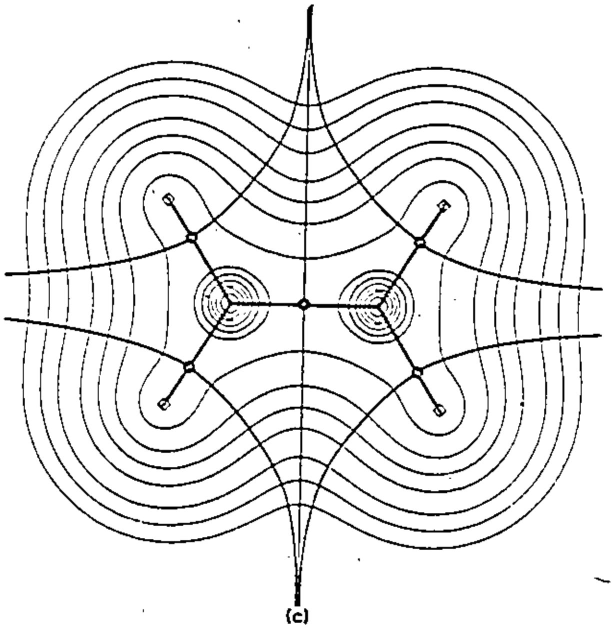
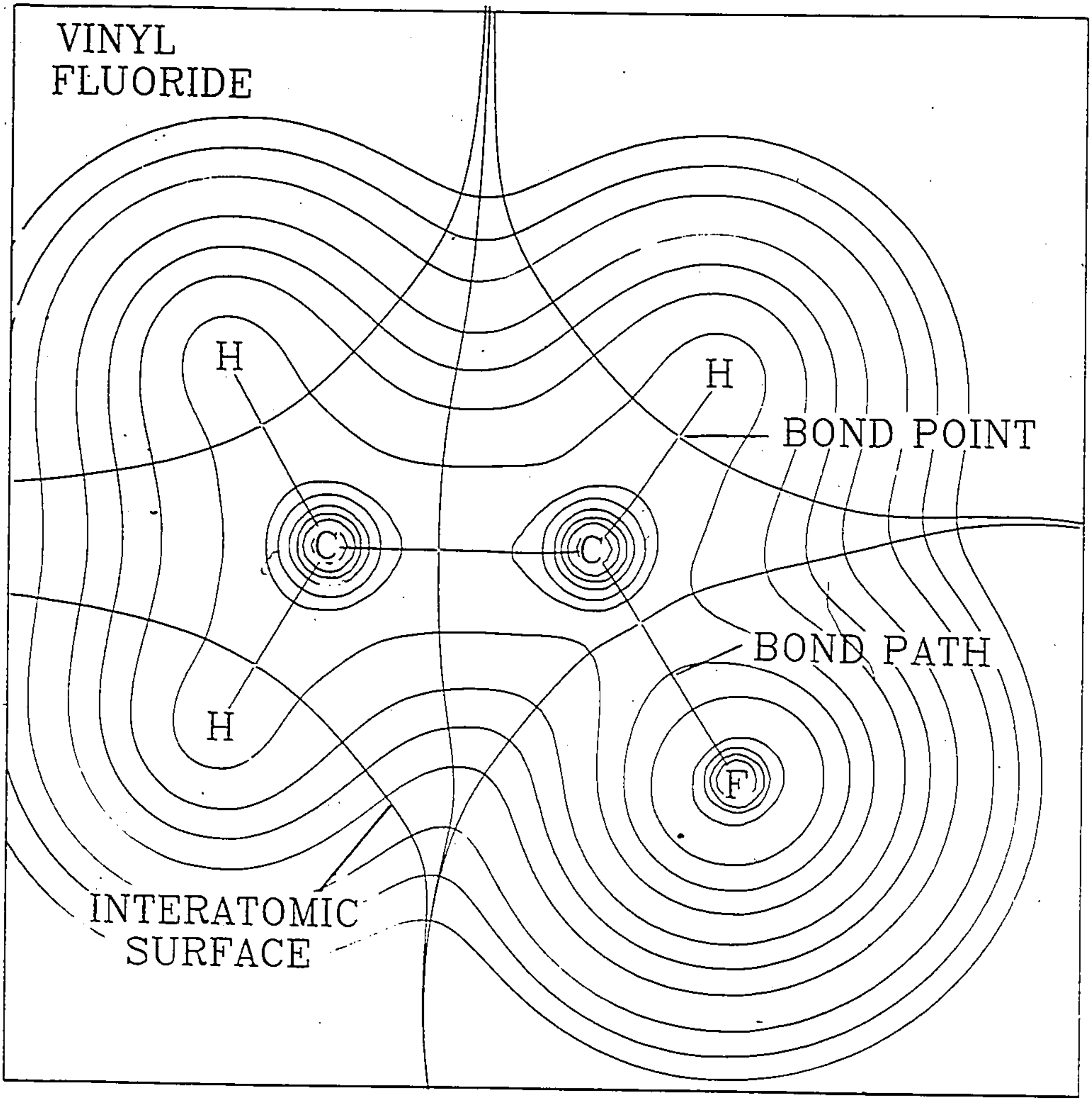


(c)

Figure 1.1.3

The molecular graph of fluoroethene superimposed on a contour map of the electron density in the molecular plane, from Slee (1986). As in ethene, the only maxima occur at the nuclei, which are marked with their chemical symbols. The "ridges" between bonded nuclei are the bond paths and the lowest point on the ridge is the (3,-1) critical point, also called the bond point. The interatomic surface dividing neighbouring atomic basins consists of the lines of steepest descent from the bond point.


VINYL
FLUORIDE
H
H
C
C
H
H
F
BOND POINT
BOND PATH
INTERATOMIC
SURFACE

assigned to the "topological" atoms defined above? To what extent do these properties mimic those expected on the basis of traditional models? These questions are taken up in Sections 1.2 and 2.1, and for the moment I shall turn to another topic and investigate the question of whether other basic qualitative concepts of chemistry also find analogues in the electron distribution.

The Topology of the Laplacian of the Charge Distribution.

The discussion above showed that the most basic concepts of chemistry find their analogues in the charge distribution, and that the influence of the nuclear—electron attraction is too great for more subtle structural features to be evident in the topology of the charge density. If we are to look for density analogues of other, less gross, chemical concepts there are two alternatives, both of which will be pursued in this thesis. One is to look at quantitative changes in atomic and critical properties and to relate such changes to chemical concepts. A second is to look at a field related to the charge density which reveals more of the fine structure of the molecule. This second possibility can be pursued by a study of the Laplacian of the charge density, which acts so as to magnify the unevennesses in the electron distribution and to reveal features which are not apparent in the density itself. Taking derivatives of a function increases the number of nodes, of maxima and of minima in that function. The second derivative of a function f(x) that falls monotonically to zero as x goes to infinity (a one dimensional analogue of a charge distribution) may show maxima and minima, as well as positive and negative values, which tell us about the local

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inhomogeneities in f(x). Such a function and its second derivative are shown schematically in Figure 1.1.4. If the second derivative is positive, then the value of f at x is less than its average at neighbouring points, while if the second derivative is negative f(x) is greater in value than the average of neighbouring points. In a region of positive $f''(x)$ f may be called "locally depleted" or "locally diluted", and conversely in a region of negative $f''(x)$, f may be called "locally compressed" or "locally concentrated". These names will be used on occasion throughout this thesis when discussing the Laplacian of the electron density, sometimes with the prefix "locally" dropped. The precise meaning of the term is simply to indicate the sign of the Laplacian of the charge density.

It is the purpose of this section to describe the form taken by the Laplacian of the charge density in molecules. It is convenient to define the negative of the Laplacian distribution,

$$L(x) = -\nabla^2\rho(x)$$

for then a region where charge is "locally compressed" has a positive value of L, while if charge is locally depleted L is negative, which is pedagogically more satisfying than to discuss $\nabla^2\rho$ directly. The Laplacian for an isolated oxygen atom is shown in Figure 1.1.5. It takes the form of a series of concentric shells. If we consider a spherical "Laplacian shell" to consist of a region where L(x) is positive (indicated by dashed contour lines) surrounded by a region where L(x) is negative (indicated by continuous contour lines), then the number of Laplacian shells is equal to the number of shells that are partially or fully occupied within the orbital model of electronic structure. This

Figure 1.1.4

A monotonically decaying, but somewhat uneven function f(x) is shown in Figure (a). Topologically, it has only a single maximum at x=0 and so is indistinguishable from a smoother function where f(x) is concave upwards for all values of x.

Figure (b) shows qualitatively the second derivative of f(x), f"(x). The unevenness in f(x) shows up in the topological description of f"(x). The region between x_2 and x_4 has a negative second derivative, and this corresponds to the "lump" in f(x). The minimum in f"(x) at x_3 is the point where the curvature of f(x) is most pronounced. The regions with positive second derivative correspond to values of x where f is concave upwards, and the maxima in f"(x) at x_1 and x_5 show where this curvature is most pronounced.

The Laplacian of the charge density magnifies the unevennesses in ρ in just the same way as the second derivative of a single valued function such as f(x). Thus, regions where the Laplacian is negative can be thought of as "lumps" in the electron distribution in just the same way that the region between x_2 and x_4 is a "lump" in f(x), and the maxima and minima of the Laplacian show where the unevenness in ρ is most pronounced.

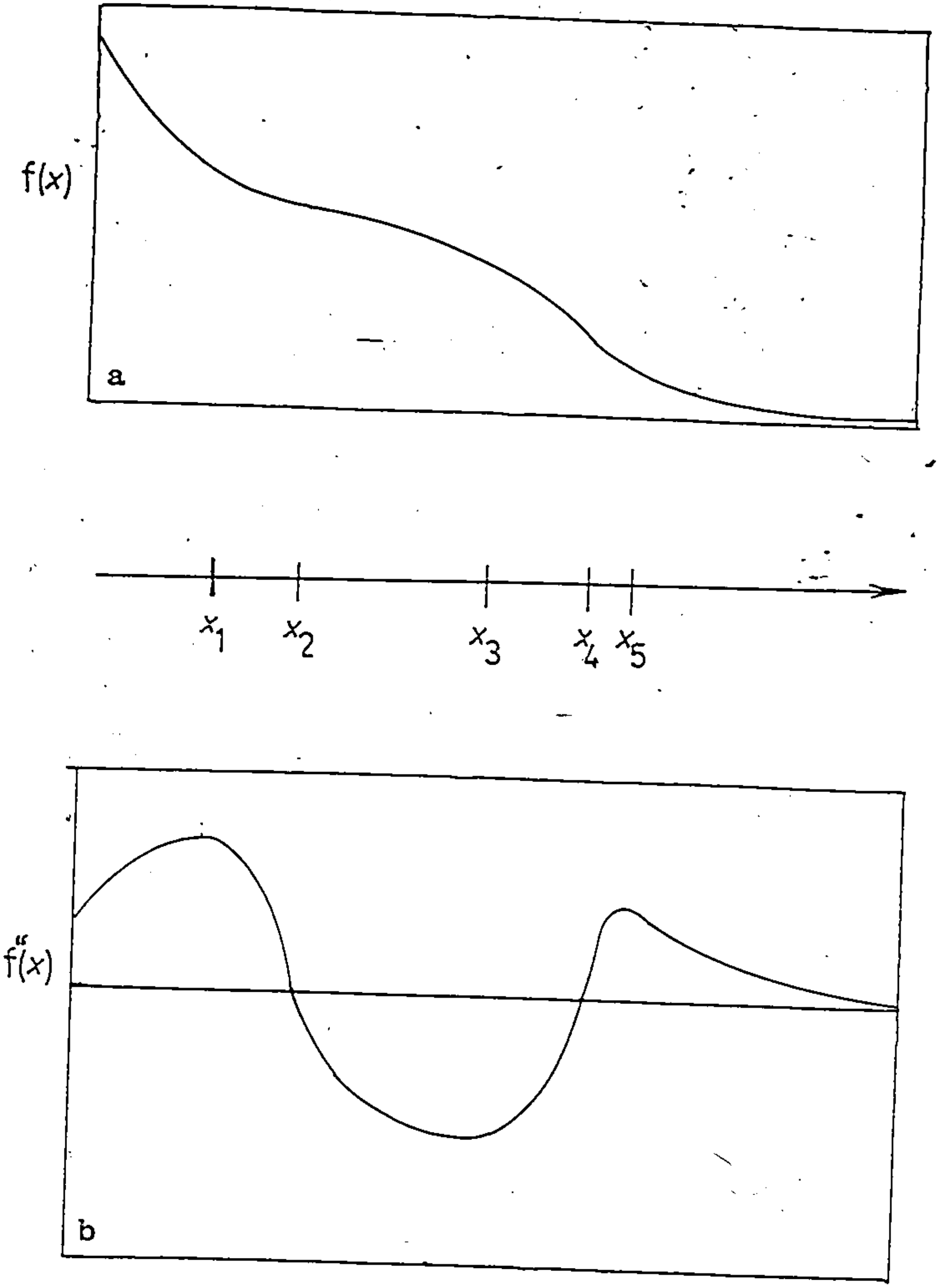
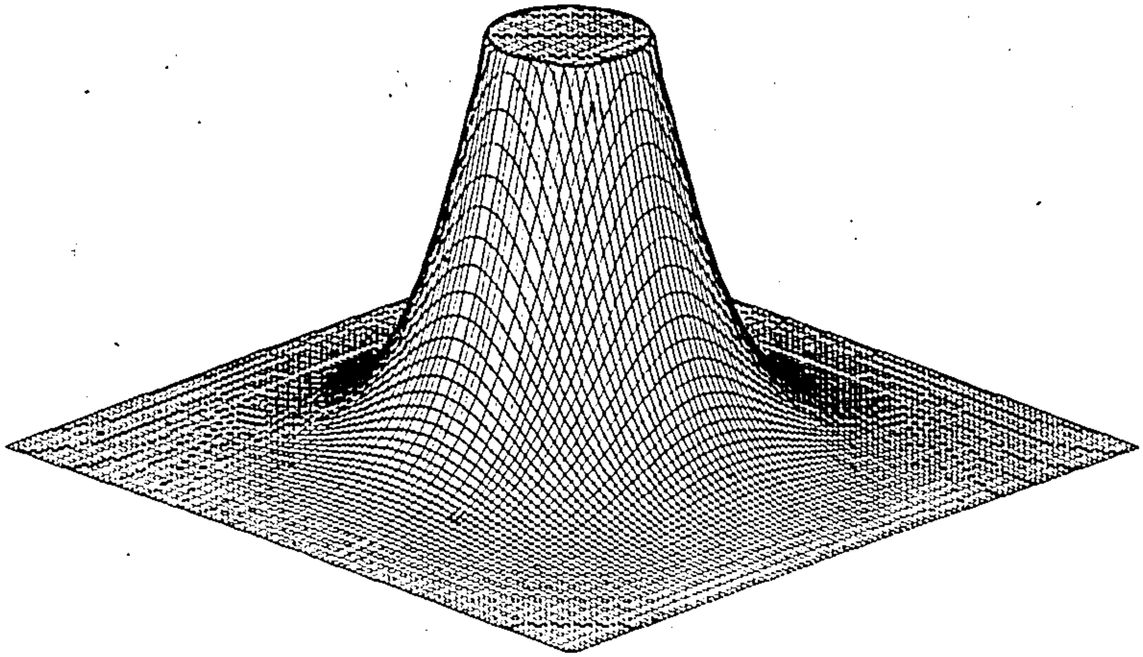

f(x)
a
x_1
x_2
x_3
x_4
x_5
f''(x)
b

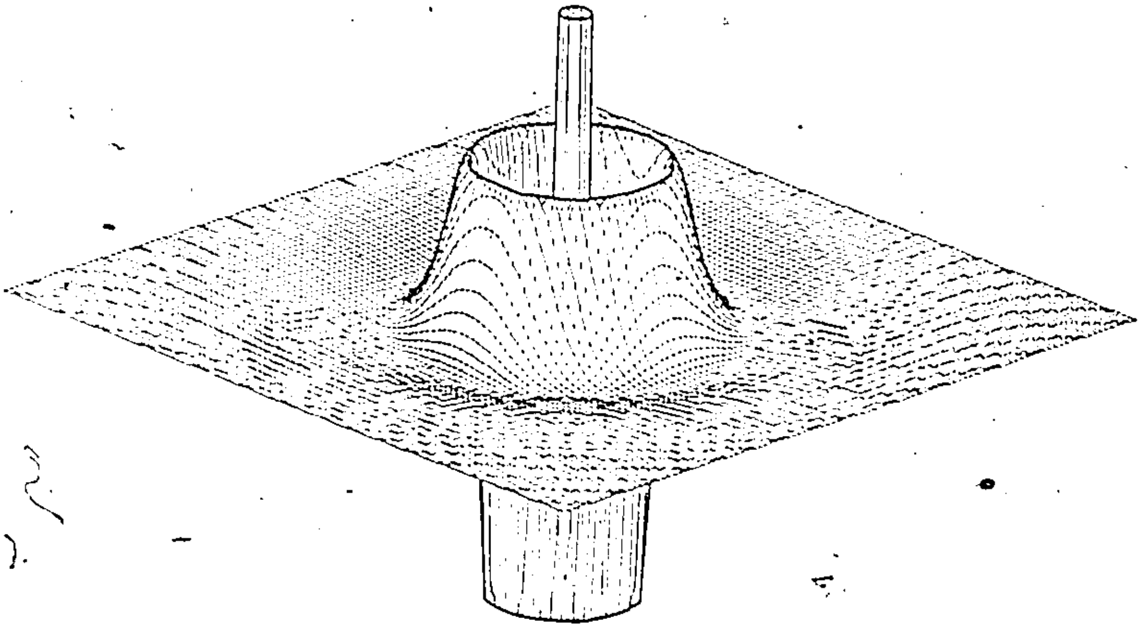
Figure 1.1.5

Relief map of the charge density of the oxygen atom and the negative of its Laplacian (L(x)), from Bader et al (1984).

As in the one-dimensional case of Figure 1.1.4, ρ is radially a monotonically decaying function, and topologically exhibits but a single maximum at the nucleus. L(x) brings out the unevenness in ρ: its "fine structure". The regions of positive L(x) correspond to "charge concentration" and those of negative L(x) to "charge depletion". The shell structure of the oxygen atom is brought out topologically by this function. There are two concentric shells, each consisting of a region of positive L surrounded by a region of negative L. This highlighting of atomic shell structure by the Laplacian of the electron density has been found to hold for most of the atoms in the periodic table (Smith et al 1985).



ρ



$-\nabla^2\rho$

equality, first explored by Bader and Essén (1984) has since been investigated by Smith and co-workers (1985) who found it to hold for almost all the atoms of the periodic table, and to be a more reliable indicator of shell structure than the commonly used radial distribution function. Both of these functions differ from the number of partially occupied electronic shells only for some of the low group number transition metal elements, but the Laplacian picks up the existence of the partially occupied shell at a smaller atomic number.

The identification of the number of Laplacian shells with the number of partially occupied electronic shells represents another density-based analogue of a chemical model. The analogue was extended to molecular Laplacian distributions by Bader and Essén (1984) and by Bader et al (1984). The Laplacian of some simple molecules is shown in Figures 1.1.6. to 1.1.10. Let us now discuss these examples. It should be born in mind that, while there are very few known exceptions to the observations made concerning the topology of ρ, the topology of L is more variable from molecule to molecule. There are, however, enough consistencies in the its behaviour to make it pedagogically useful to state some general observations first, even though these are not universal, and to point out exceptions as we proceed.

A common feature of the examples is that around each atom the number of identifiable Laplacian shells remains the same as for the isolated atom. The one exception is lithium in methyl lithium, (Figure 1.1.6) which loses its second shell. This is expected on the basis of simple orbital models of chemical bonding, which suggest that this bond should be ionic. Thus the lithium is essentially a Li^+ ion, and

Figure 1.1.6

Contour map of the Laplacian of the electron density in methyl lithium, taken from a 6-31G**/6-31G** wavefunction supplied by P. J. MacDougall. The solid lines indicate regions where L(x) is negative and the dotted lines regions where L(x) is positive. The most noticeable feature of this diagram is that lithium has only one Laplacian shell. This reflects the fact that it has essentially lost it's outer valence electron to the methyl group and can be considered as an Li^+ ion.

The L-maxima are indicated by solid squares and the (3,-1) critical points by solid triangles. Only the critical points discussed in the text are explicitly shown, though the positions of other critical points can be seen from the contours. The CH bond shows an L-maximum at the carbon end and a (3,-1) critical point closer to the hydrogen nucleus, as is usual for XH bonds. The carbon atom also has a maximum in the CLi bonding region. Although there is a hole in the valence shell of the carbon atom facing away from the CH bond, there is no such hole on the side facing away from the CLi bond.

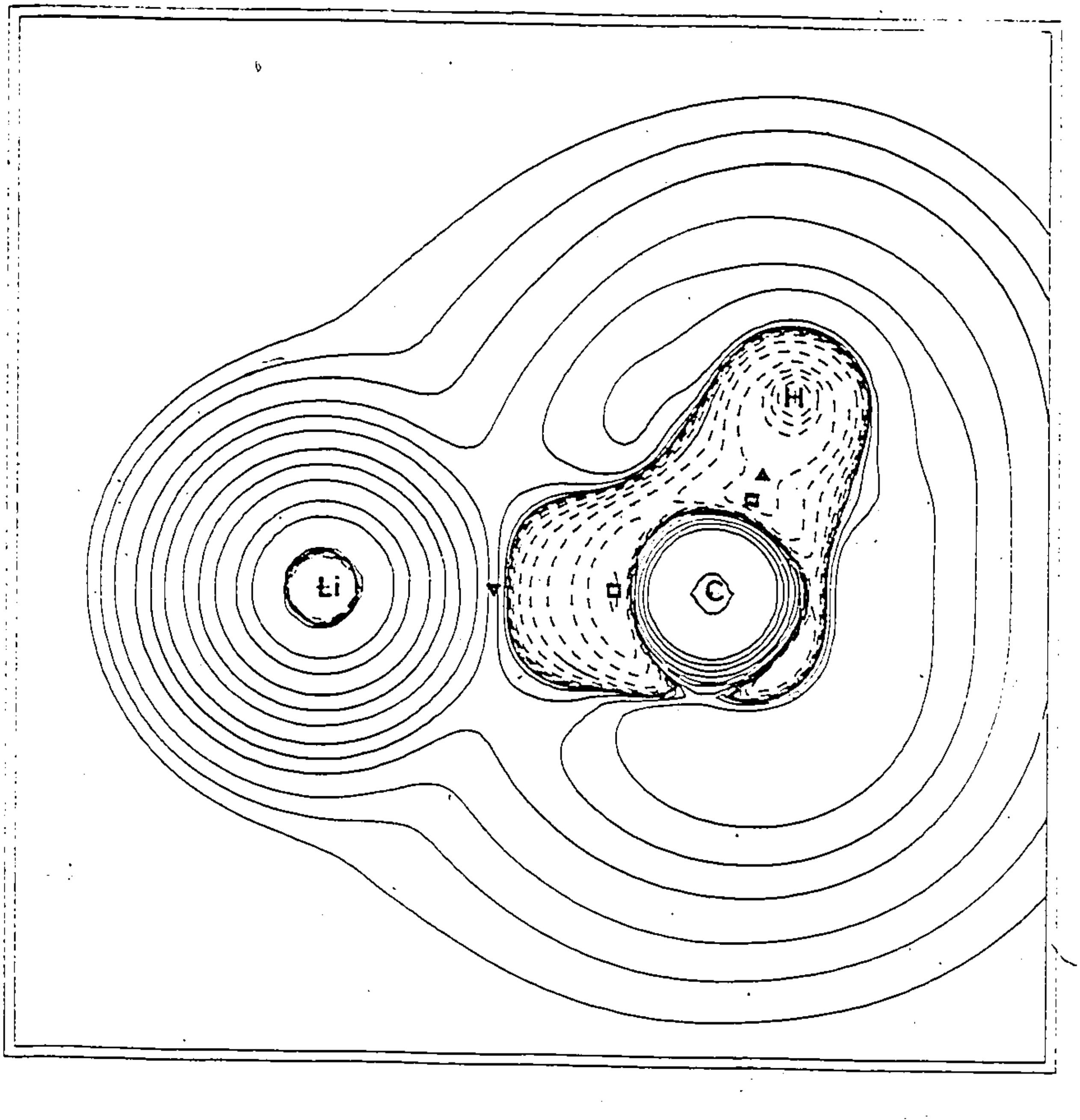

Li
C
H

Figure 1.1.7

Relief diagrams of the density and its Laplacian for the water molecule, from Bader et al (1984).

Figure (a) shows the C_2v symmetry plane, in which the density has a single maximum at the oxygen nucleus, and looks very much like the isolated oxygen atom of Figure 1.1.5. The Laplacian shows the differences between the two distributions that are not apparent from the density alone. L(x) has two maxima in the valence shell of the oxygen atom, above and below the molecular plane. These correspond to the positions of "lone pairs" in the VSEPR model. Between the two maxima are saddle points which are (3,-1) L-critical points.

Figure (b) shows the molecular plane of the water molecule. The density shows the maxima at the nuclei and the ridges of density that are the bond paths linking the oxygen and hydrogen nuclei. L(x) has a more complicated structure. The valence shell of the oxygen atoms has a local maximum along each of the bond paths to hydrogen. What appears as the third maximum is another view of the (3,-1) critical point shown in Figure (a). This makes clear the general observation that bonded charge concentrations are smaller in value than nonbonded charge concentrations.

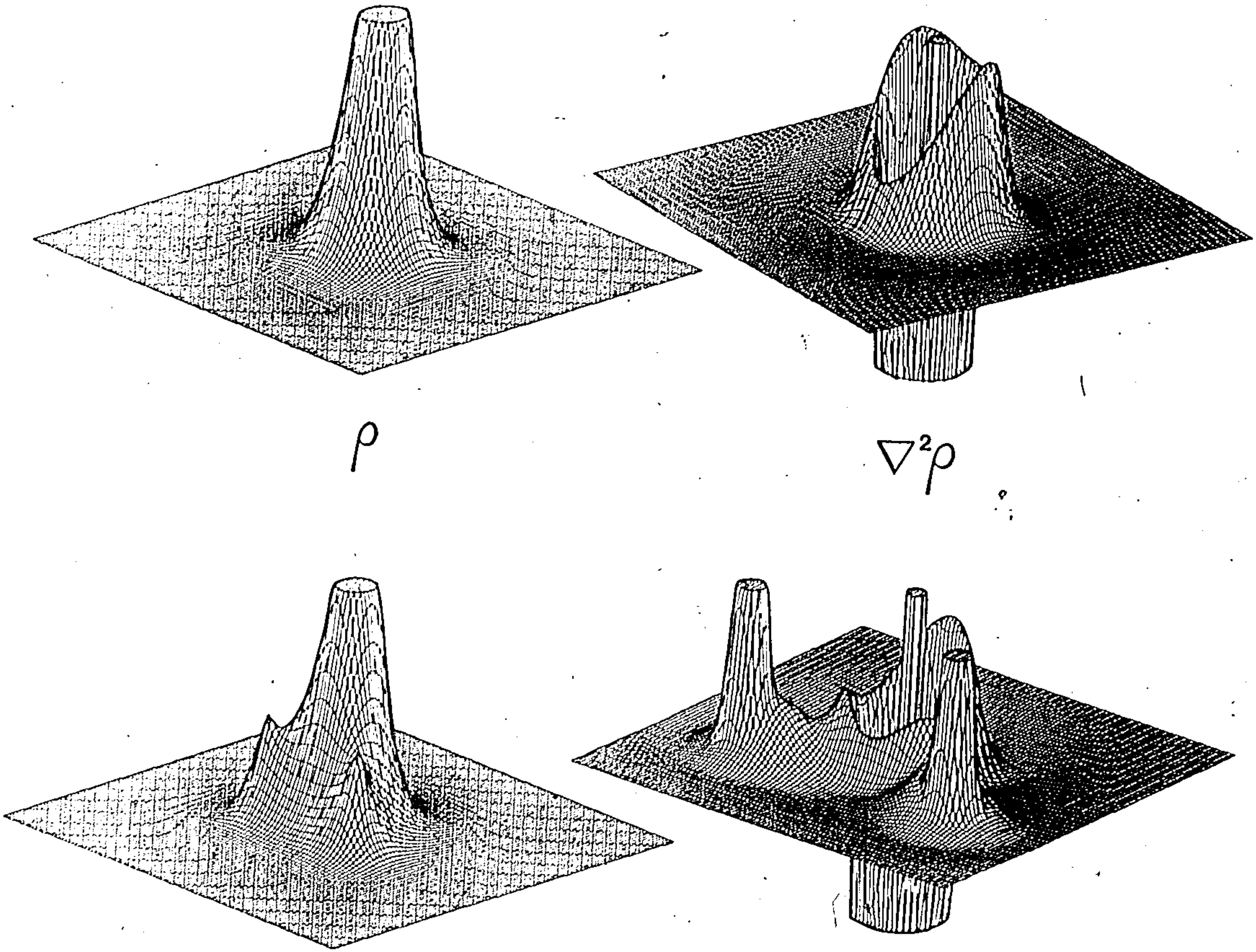

ρ
∇²ρ

Figure 1.1.8

A contour map of the Laplacian of the electron distribution for the ammonia molecule, in a plane containing the nitrogen nucleus and one hydrogen nucleus. The nitrogen atom has a maximum for each NH bond and a maximum in the nonbonded region which is larger in value. This corresponds to the arrangement of lone pairs on the basis of Lewis models or the VSEPR theory, and is analogous to the water molecule shown in Figure 1.1.7.

1.8

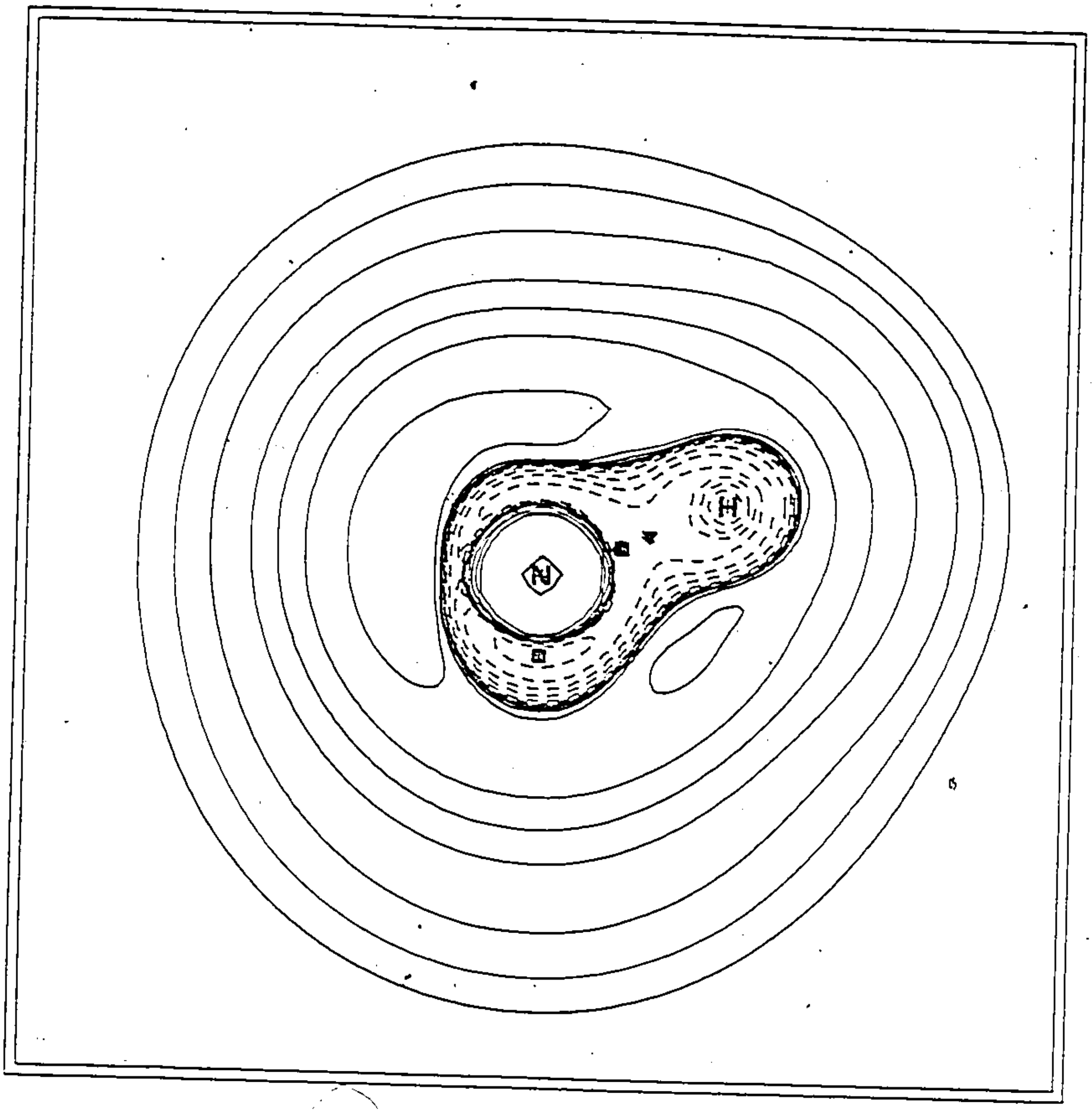
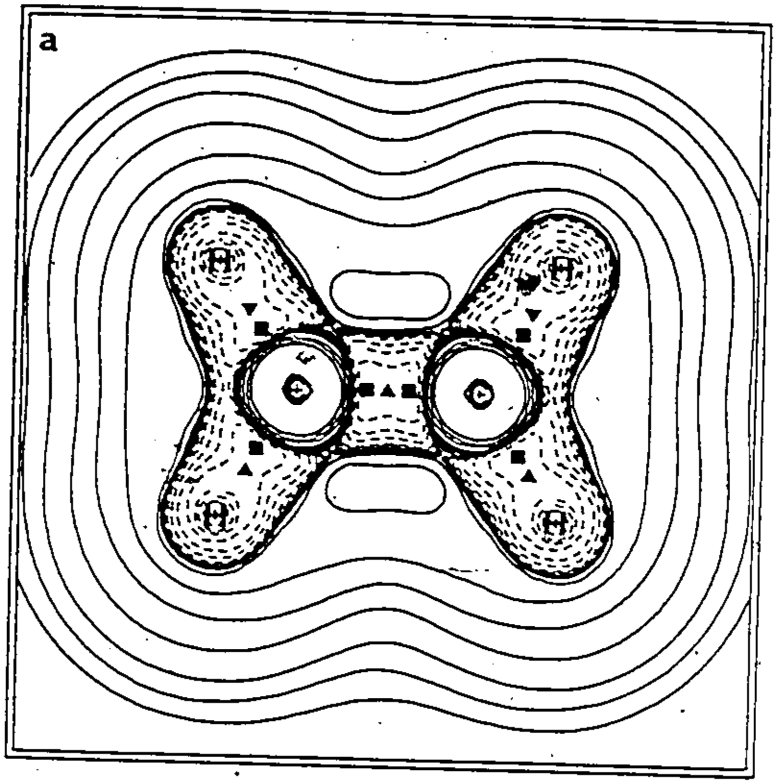


Figure 1.1.9

Figure (a) shows the Laplacian in the molecular plane of ethene. Each carbon atom has a maximum associated with each bond, and each bond also has a (3,-1) critical point.

Figure (b) shows the Laplacian in the π plane of ethene. The maxima associated with the CC bond occur in this plane as well. There are no maxima associated with the "π cloud", but there are (3,+1) critical points above and below each carbon atom which can be used to study the changes in off-axis density. These critical points are indicated by solid circles.


a
H
H
H
H

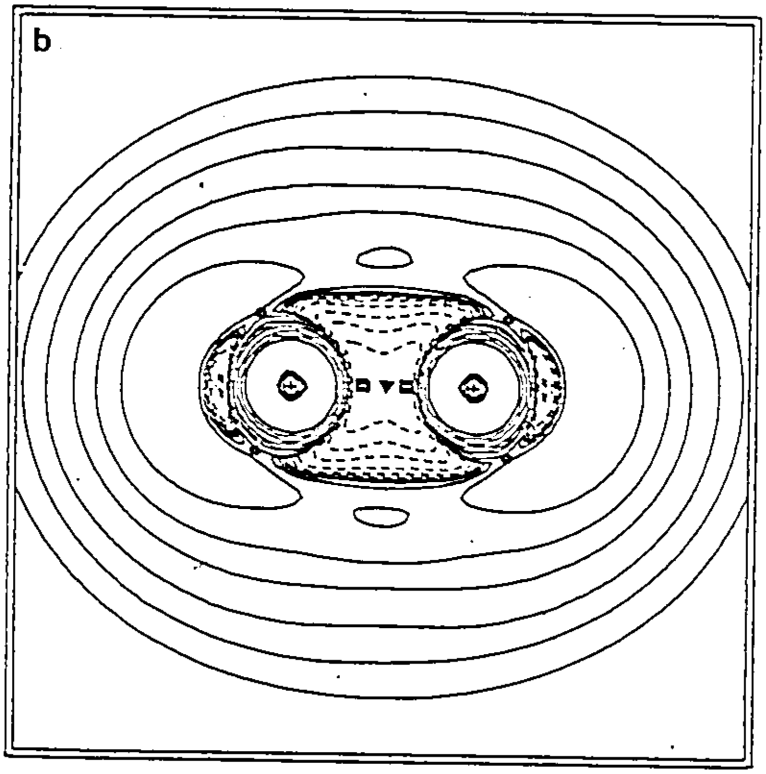
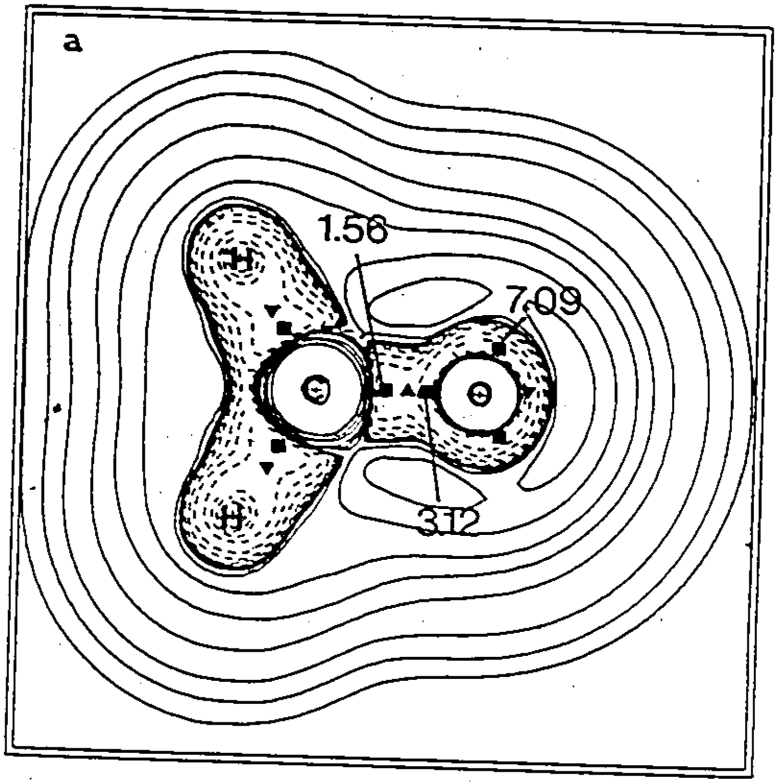
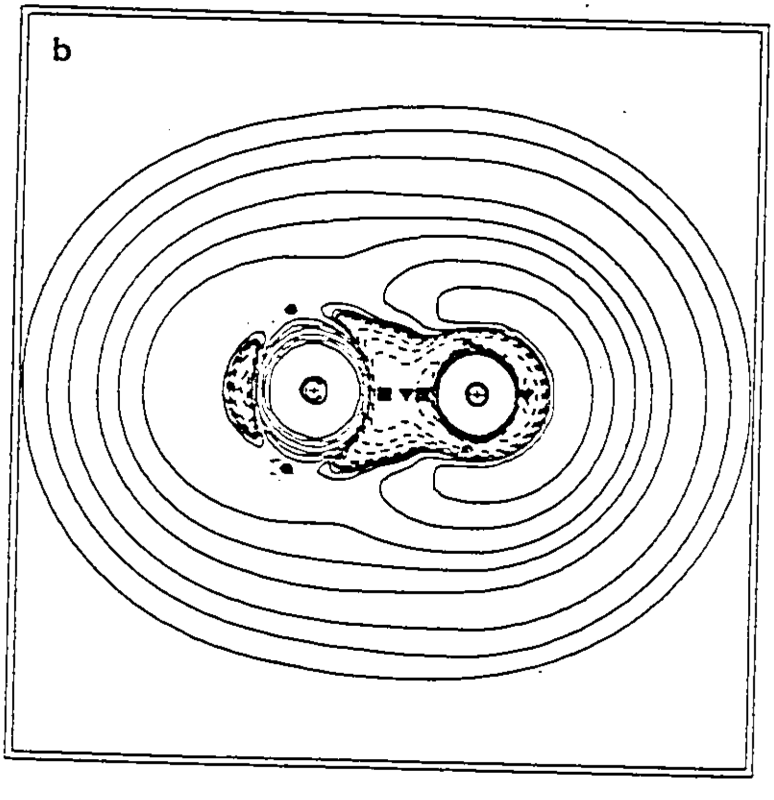

b

Figure 1.1.10

Figure (a) shows the Laplacian for the molecular plane of formaldehyde. The (by now familiar) maxima occur around the carbon atom in the valence shell, one associated with each bond. The topology of L around the oxygen atom is interesting: there are two maxima (solid squares) in the "lone pair" regions of the VSEPR model and one smaller maximum associated with the CO bond. The values of L at these L-maxima are indicated in atomic units (a_0^{-5}). Linking these maxima are (3,-1) critical points.

Figure (b) shows the Laplacian in the π plane of formaldehyde. There are no non-bonded maxima around the oxygen atom in this plane, only saddle points. Within the VSEPR model this corresponds to a sp^2 hybridised oxygen atom. The (3,+1) critical points associated with the π bond in ethene appear in the formaldehyde molecule as well: above and below both the carbon and the oxygen nuclei. The value of L at the oxygen (3,+1) critical point is positive, while that at the carbon (3,+1) point is negative, corresponding to the expected polarity of the π bond.


a
H
H
1.56
7.09
3.12


b

consequently has only one shell. The Laplacian shells are distorted from spherical symmetry by the lower symmetry of their environment, and within each shell isolated critical points appear. It is convenient to label these as critical points in $L(x)$ rather than in $\nabla^2\rho(x)$. The Laplacian shell of most interest to us in finding analogues of chemical models is the valence shell, and from now on I will restrict my discussion to this. In particular, I will look at the positive L region of the valence shell (ie, dashed contours), as this provides all the information needed. This region was called the "valence shell charge concentration" by Bader et al (1985), abbreviated to VSCC.

First consider the arrangement of maxima in L in the VSCC. The oxygen of water is shown in relief in Figure 1.1.7. It has four maxima (in L) in its VSCC, one close to each bond path, and two, above and below the molecular plane, on radii pointing into the non-bonded region, the arrangement being roughly tetrahedral. The positions of the L-maxima around oxygen correspond closely to the anticipated positions of the lone pairs and the bonded pairs within the Valence Shell Electron Pair Repulsion (VSEPR) model of molecular geometry (Gillespie, 1972). The angle between the "bonded L-maxima" is 103.1°, while that between the nonbonded L-maxima or "lone pair L-maxima" is 138.3° (Bader et al 1984). The analogy between maxima in $L(x)$ and VSEPR concepts, in particular the idea of lone pairs, is particularly striking since no features of electron densities have been found previously which correspond to these notions.

Ammonia follows the same pattern as water, with each bond showing an L-maximum at each end, and with one "lone pair" on nitrogen in the appropriate position. Figure 1.1.8 shows the Laplacian in a plane of the ammonia molecule as a contour map. Ethene (Figure 1.1.9) shows two L-maxima in the molecular plane along the bond path, but there are no L-maxima above and below the plane of the nuclei. There is no difference in the topology of the Laplacian in the bonding region between ethane and ethene. Formaldehyde (Figure 1.1.10) again exhibits two L-maxima for each bond path and the oxygen shows L-maxima in the molecular plane, at angles of 107.4° to the OC bond, in approximately the position expected for the VSEPR lone pairs in this molecule. (VSEPR suggests that the lone pairs on the assumed sp^2 oxygen will occupy more space than the bonded pair, and so the angle between them will open out to more than 120°, closing the angle with the CO bond to less than 120°).

Thus, in the case of σ bonds and lone pairs at least, the analogy between Lewis electron pair concepts as refined by the VSEPR theory and the topology of the Laplacian holds well, although no L-maxima occur which correspond to the π bonds of simple orbital models. Bader et al (1984) have shown that the analogy is more general, and persists in such compounds as ClF_3 in a variety of geometries, as well as SF_4 and ClF_5. A recent study of three membered ring systems by Cremer and Kraka (1985a, b) has extended the correspondences between VSEPR concepts and the topology of the Laplacian to these systems also.

There is one exception to the analogy which should be noted. In bonds between carbon and very electronegative elements there is often no L-maximum at the heteroatom end of the bond. Instead a critical point of lower signature in L is sometimes found, as in the case of methyl fluoride.

The value of L at its maxima are indicated in Figure 1.1.10 for formaldehyde. It can be seen that "lone pair" L-maxima possess much larger values than bonded L-maxima, a result that applies to all the other examples as well. Also, within a bond, the relative values of L appear to indicate the polarity of that bond with the critical point of larger L being at the negative end of the bond.

Let us now turn our attention to other features of the topology of the VSCC. There are saddle points of both (3,-1) and (3,+1) types that link the L-maxima. No L-minima are found in general, as the VSCC is a radial L-maximum so that all critical points in the VSCC have at least one negative eigenvalue. As an example, the critical points above and below the molecular plane in ethene, close to each carbon atom, are (3,+1) L-critical points and so represent radial L-maxima, but L-minima in the VSCC surface. It should be noted that L is negative at these points: the valence shell of carbon has been disrupted enough to break the continuous region of positive L that surrounds the bare carbon atom. The remnants of a "shell" still remain, however, as L has a radial maximum at this distance even though it is negative in value. There are no L-maxima above and below the plane that correspond to the "π bond", which emphasises the fact that the σ and π distributions occupy the same region of space: there is no spatially separate π cloud (Coulson et al 1952). Instead, the (3,+1) critical points appear to be the only L-critical points which may carry information about the behaviour of the density in the π plane off the internuclear axis. These critical points are studied for a series of ethenes in Chapter 3.

The π plane of formaldehyde shows that (3,+1) L-critical points are present again, in a similar arrangement to those in ethene above and below the carbon and oxygen. At the oxygen end the value of L is positive, while at the carbon end it is negative, reflecting the expected polarisation of the π bond. Thus, the (3,+1) critical points do seem to indicate the existence and polarity of π bonds. For this reason I will refer to them as "π critical points" in L.

The study of the topology of the Laplacian is at an early stage, and there are many areas of potential interest to be explored. For example, no significance has yet been assigned to the many basins it exhibits, and only the most obviously significant critical points have been investigated: the L-maxima in the VSCC and the (3,+1) L-critical points in the π plane of unsaturated systems. Further, although a theory has been developed which shows the quantum mechanical significance of atomic basins, no such theory has yet been developed which shows that any particular significance is to be attached to topological features of the Laplacian. The relationship between chemical concepts and the Laplacian is still at an empirical, observational level, although further studies of the correspondence between the two may yield valuable insight into molecular reactivity (Bader and MacDougall 1985). The formal quantum theoretical basis for the study of the topological elements of the charge distribution itself is, however, thoroughly developed and is presented in the following section.

1.2 THE QUANTUM MECHANICS OF SUBSYSTEMS

The definition of the atom as a bounded region of space prompts the question whether such a region can have mechanical properties assigned to it. This section develops the formal basis for the definition of regional properties by generalising the variational principle and the hypervirial theorem to apply to bounded regions of space, together with the virial theorem and the Ehrenfest force law. It is shown that only for regions over which $\nabla^2\rho$ integrates to zero do the virial theorem and the expression for the variation of the energy functional have an unambiguous form. It is also shown that the total energy of a system can be partitioned into a sum of contributions from distinct regions of space in a meaningful manner if the energy is defined in terms of the virial theorem.

Only for regions over which the integral of $\nabla^2\rho$ vanishes can such an energy be uniquely defined, and hence such regions are called <u>quantum subsystems</u>, a name that will be used throughout the section for convenience, even though the demonstration of their uniqueness takes place toward the end. In the framework of molecular quantum mechanics, the only quantum subsystems that contain a single nucleus are observed to be the topologically defined atoms described in Section 1.1, and so the results of this section constitute the quantum mechanical basis for the definition of an atom in a molecule and its properties. These results have all been derived previously (Srebrenik and Bader 1975, Bader and Nguyen-Dang 1981), although the derivations presented here are slightly different to the original approach. The time-dependent case has also been studied by a generalisation of the Schwinger's principle of stationary action (1951) to bounded regions of space (Srebrenik et al 1978): again, quantum subsystems are the only regions to which the principle generalises in an unambiguous manner. As only stationary state problems occur in this thesis I will not discuss the time-dependent case.

To demonstrate the variational properties unique to quantum subsystems I will first review the way in which variational or stationary principles can be used to derive special theorems, such as conservation laws, that are satisfied by dynamical systems. The ways in which the Schrödinger equation, the hypervirial theorem, the Ehrenfest force law, the Hellmann-Feynman theorem and the virial theorem for a total system are derived from the variational principle are then reviewed. The variation of a projection of the energy functional onto a bounded region of space is outlined, and the regional forms of the theorems satisfied by variational wavefunctions are derived. These regional theorems are also approached from another angle, starting from a local description of a system based on the equation of continuity (Messiah 1967, v. 1, p.121). The definition of the energy of an atom in a molecule is discussed to finish the section.

Variational Principles and their Generalisations in Classical Mechanics.

Stationary principles provide a concise and general way of expressing the physical laws governing the behaviour of a particular system, whether that system be described by classical, relativistic, or quantum mechanics and whether it be particulate or continuous in nature (Moiseiwitsch 1966, Katz 1965, Yourgrau and Mandelstam 1968). As prologue to the (non-relativistic quantum) variational principle I will review briefly the derivation the equations of motion for a classical system of particles from the action principle and show how the momentum of such a system can be defined and the conservation laws derived from the variational approach (Katz 1965, Chapter 1). The philosophy and techniques of this section are very similar to those used to define properties and special theorems for regions of space within quantum mechanics.

The classical action principle states that the generalised coordinates (q) and conjugate momenta (p) of a classical system behave such as to make the "action integral"

$$W = \int dt\,\mathcal{L} = \int dt\,(p\,dq/dt - H(q,p,t)) \qquad [1.2.1]$$

stationary with respect to any variation of the p's and q's. $\mathcal{L}$ is the Lagrangian of the system, and although it can be taken as the fundamental dynamical quantity, it is more appropriate in the present context to take the related quantity H, the Hamiltonian of the system, as fundamental. H is simply the sum of kinetic and potential energies of the system for conservative systems, which cover all cases of interest to the present work. The problem of finding a differential condition such that this integral is made stationary (i.e. of finding the equations of motion of the system) can be solved using the calculus of variations. In this case, treating the q's and p's as independent variables, the calculation goes as follows:

$$\delta W = \delta\int dt\,(p\,dq/dt - H(q,p,t)) = 0$$

$$= \int dt\,(\delta p\,dq/dt - \delta p\,\partial H/\partial p + p\,d(\delta q)/dt - \delta q\,\partial H/\partial q)$$

$$= \int dt\,\delta p(dq/dt - \partial H/\partial p) + (p\delta q)\Big|_{t_0}^{t_1} - \int dt(dp/dt + \partial H/\partial q)\delta q \qquad [1.2.2]$$

If we require the variation of q to vanish at the time end-points then

Hamilton's equations of motion follow:

$$\partial H/\partial p = dq/dt \qquad -\partial H/\partial q = dp/dt \tag{1.2.3}$$

A generalisation of this result is obtained if the condition that $\delta q=0$ at the time end-points is relaxed. The condition for the equations of motion to be satisfied is now that the variation of the action integral yield only contributions from the time end-points, rather than that it be stationary. The purpose of this generalisation is that it permits the derivation of conservation laws as well as equations of motion directly from the action principle. Also, dynamical quantities can be defined in terms of different choices of generators of variations. One example gives the essentials. The generalised action principle reads that, when the equations of motion are satisfied,

$$\delta W = p(t_2)\delta q(t_2) - p(t_1)\delta q(t_1) \tag{1.2.4}$$

Suppose we choose position in space as the generalised coordinates and choose a constant translation as the variation:

$$\delta q(t_2) = \delta q(t_1) = \delta q \tag{1.2.5}$$

then the action principle yields

$$\delta W = (p(t_2) - p(t_1))\delta q \tag{1.2.6}$$

Now, if the action integral is invariant with respect to δq, which is the case when the problem has translational symmetry, δW must vanish and hence $p(t_2) = p(t_1)$: momentum is conserved as a consequence of the invariance of the action integral to a shift in coordinate origin. If a time-dependent translation is considered instead, then equation [1.2.4] shows that the difference in momentum at the time end-points is "generated" by the motion. In cases where H is known, but p is not, this can serve to define the momentum of the system. Other dynamical properties of the system and other conservation laws can be derived by the same approach using other choices for the variation.

Specification of the equations of motion (and, in quantum mechanics, the commutation relations) serves to define the mechanics of the system as completely as does the action principle, yet the latter has the property that all the dynamics of a system can be seen to unfold from a single postulate. This unity is a not inconsiderable advantage: in the late nineteen forties it was the development of an action principle formulation of relativistic quantum mechanics independently by Feynman, Schwinger and Tomonaga that laid the foundations for the correct formulation of quantum electrodynamics (Schwinger 1958). All formulations of mechanics are equivalent, but some are more equivalent than others.

The All-Space Variational Principle in Quantum Mechanics.

The non-relativistic, time-independent Schrödinger equation can be derived from a variational principle (see, eg, Epstein 1974a). In this case there is no need to impose the requirement that variations vanish at infinity, as all normaliseable wavefunctions vanish there anyway, so no surface contributions to the variation can arise. A variety of formulations of the variational principle exist, but this is not a survey of the method and so it will suffice to take a single approach. The expectation value of the Hamiltonian is written as

$$E[\phi] = \int d\tau\ \phi^*(H-\lambda)\phi \equiv (\phi,(H-\lambda)\phi) \qquad [1.2.7]$$

where for molecular problems H is the electronic Hamiltonian for an N electron system in the field of N_α nuclei:

$$H \equiv T_e + V_{ne} + V_{ee} + V_{nn} = T + V \qquad [1.2.8]$$

λ is a Lagrange multiplier, and a scalar product notation is being used as it is convenient in the treatment of the quantum mechanics of regions of space. The scalar product has the properties that

$$(\alpha\phi_i,\phi_j) = (\phi_j,\alpha\phi_i)^* = \alpha^*(\phi_i,\phi_j) \qquad [1.2.9]$$

where α is a number. Throughout this chapter the N-electron wavefunction ϕ will be chosen to be normalised to unity.

E[ϕ] is varied by applying an operator δ to the state vector. If δ is considered to be a general variation of ϕ, which alters some or all of a set of parameters on which ϕ depends, then the variation of the energy functional is defined as

$$\delta E[\phi] = (\delta\phi,(H-\lambda)\phi) + (\phi,(H-\lambda)\delta\phi) \qquad [1.2.10]$$

The variational principle states that the correct ϕ is that for which

$$\delta E[\phi] = 0 \qquad [1.2.11]$$

or equivalently,

$$(\delta\phi,(H-\lambda)\phi) + (\phi,(H-\lambda)\delta\phi) = 0 \qquad [1.2.12]$$

or, using the hermiticity of H

$$(\delta\phi,(H-\lambda)\phi) + ((H-\lambda)\phi,\delta\phi) = 0 \qquad [1.2.13]$$

The expression for the variation of the energy functional can be written in another way which, although not of immediately apparent usefulness, will be of use later. If δϕ is a valid variation of the wavefunction, then so is $\delta'\phi = i\delta\phi$. Replacing δ by δ' in equation [1.2.12] and dividing by i, enables the variational principle to be written as

$$\delta E = -(\delta\phi,(H-\lambda)\phi) + (\phi,(H-\lambda)\delta\phi) = 0 \qquad [1.2.14]$$

Schrödinger's equation can be derived from equation [1.2.13] if it is noted that the variations of ϕ and of ϕ^* can be treated as independent. This occurs because the quantity $\delta\phi$ is a complex function comprised of two real valued functions, $(\delta\phi)_R$ and $(\delta\phi)_I$: each of which can be independently varied. An alternative to viewing $(\delta\phi)_R$ and $(\delta\phi)_I$ as the independent variables is to view $(\delta\phi)$ and $(\delta\phi)^*$ as the independent quantities (Epstein 1974a). The Schrödinger equations follow:

$$H\phi = \lambda\phi, \qquad H\phi^* = \lambda\phi^* \qquad [1.2.15]$$

The variational principle also leads to the hypervirial theorem (Hirschfelder 1960, Epstein 1974a), a general result which states that the expectation values of commutators of a broad class of observables with the Hamiltonian vanish. The hypervirial theorem contains as special cases the virial theorem, and Ehrenfest's force law for a stationary state.

A special class of variations is of particular interest: those which result from the application of an operator δ on ϕ defined by

$$\delta\phi = i\varepsilon A\phi \qquad [1.2.16]$$

where A is a hermitian operator and ε is an infinitesimal real quantity, so that the hermitian conjugate of δ is given by

$$\delta^+\phi = -i\varepsilon A\phi \qquad [1.2.17]$$

It can be seen that (1+δ) is a unitary operator, as the second order terms in ε can be ignored: