

Chapter 1

How Science Deals with Complex Problems

The theory of the electronic structure of molecules is like many problems in science; the basic laws underlying the problem are very well known but the way in which these laws are to be applied to yield results which are meaningful in a particular context is not obvious. This situation is, perhaps, most familiar in the application of Newton's mechanics to the motions of the solar system. Just as it is not possible to predict the number of satellites which actually orbit Jupiter, we cannot obtain a description of the electronic structures of molecules solely from the basic laws, we must supply additional ideas from a knowledge of the chemistry involved. The main idea used here is the breakdown of the overall system into a series of interacting sub-systems

Contents

1.1 Introduction: Levels in Science	2
1.2 What are Molecules Made Of?	4
1.3 Interactions Between Atoms	6
1.4 The Simplest examples: H₂ and LiH	8
1.4.1 The Hydrogen Molecule	8
1.4.2 The Lithium Hydride Molecule	10
1.4.3 Comments on H ₂ and LiH	15
1.5 How to Proceed?	16

1.1 Introduction: Levels in Science

It is commonly said that Newton's laws give an essentially perfect description of the internal motions of the solar system; the motions of the moons around the planets and of the planets around the sun. There is similar confidence among some physicists that Schrödinger's mechanics (quantum theory) is capable of providing a complete quantitative account of chemical phenomena. Both of these opinions are wrong. The ways in which they are wrong is as important to understand as the sense in which they are thought to be right.

Let's see what would be involved in calculating the orbits of the various bodies in the solar system. We would need:

- Newton's laws of motion (principally $F = ma$)
- The number of bodies and their masses (sun, planets, moons, main asteroids—ignore small bodies and dust *etc.*)
- The law of interaction between the bodies (gravity, just depending on the masses of the bodies and their distances apart)

We have all this information so we can now set to and calculate the paths of all the bodies in the solar system.

Compare this with the information needed to calculate the distributions and energies of the electrons in (say) the ethanol molecule:

- Schrödinger's laws of motion (the Schrödinger equation)
- The number of bodies, their masses and charges (nuclei and electrons)
- The law of interaction between bodies (electrostatics, Coulomb's law of attraction and repulsion)

Again, all this information is known so we can go ahead and calculate everything about the ethanol molecule.

The two cases are remarkably similar: a few dozen bodies, a known law of interaction between them and the correct laws of motion. But in neither case can we actually go ahead and get the desired result because we do not know how the systems of bodies are *organised*. In order to even begin we need to know lots of “large-scale” information; for example,:

- How many moons each planet has
- The connectivity of the ethanol molecule (which atoms are “bonded”)

What is common to both cases is the fact that each of these relatively simple mechanical systems is, in fact, composed of a number of smaller sub-systems and it is precisely the way in which the overall systems are broken down into smaller sub-systems which must be known before a detailed account of the motion can be even attempted. For example, I am sure that there will be thousands of possible solutions of Newton's equations where the planets have no moons and all the bodies orbit the sun as planets; conversely there will be solutions of the dynamical equations where Venus has a moon and Mars has none and many, many more in addition to the actual, real case.

However, what *is* true is that (in both the solar system and the molecule), *when the breakdown of the whole system is known* and the correct mechanics is applied to the sub-systems the motions of the sub-systems and hence of the whole system can be calculated with great accuracy. In other words, when studying any system of even moderate complexity, a great deal of information is required at what one might call a "high" level before one can even think about applying the basic, "low-level" laws which are commonly said to be able to explain the structure and motions of the system.

The upshot of these considerations is that, in any science which is not concerned with the most basic phenomena, there is an all-important analysis to be made before any quantitative calculations can be attempted. The system under study must be analysed into the essential sub-systems of which it is composed. Now here's the problem: how do we decide which are these "essential" sub-systems into which the whole system may be divided in the most useful and revealing way? In the case of the solar system the analysis is easy, partly because we can literally see what the most useful sub-systems are: we simply take a telescope and see that (for example) Jupiter *and all its moons* orbit the sun together *as a group* while simultaneously undergoing their own "local" internal motions (the moons orbiting the planet). The situation is similar for all the other planets; they are either orbiting alone or taking their moon(s) with them. So, we might take the following strategy:

- Use the mass of each planet together with its moons and use Newton's equations to calculate the orbit of this whole group around the sun ignoring the other planetary groups.
- Then calculate the orbits of the moons around each planet ignoring the sun and the other planetary groups.
- Finally calculate the mutual interactions amongst the planetary

groups—how Jupiter influences the motion of Saturn and its moons *etc.*

The whole idea being to divide the system up into sub-systems which are mutually interacting but in a way that gives a good deal of *independence* to each sub-system so that they are recognisable as sub-systems whose motions are not completely disrupted by the presence of the other sub-systems; the orbit of the moon round the Earth *is* affected by Jupiter but not much.

This analysis into substructures has to be carried out even if no actual detailed calculations are to be done; breaking down a complex structure into its component parts is the way we *actually think* about these structures; no-one pictures the solar system in their minds as just a set of dozens of bodies nor do they picture a molecule as just a collection of electrons and nuclei.

This is all, of course, very obvious because of the clear distinction between the planetary groups and the enormous distances between them. But what about the problem of the motions of electrons and nuclei in a molecule? All this complicated motion occurs in a very small region of space and all the bodies are *charged* and the interactions amongst charged particles are billions of times stronger than gravitational interactions.

We have to decide what are the optimum subsystems into which a molecule is to be divided. In other words “What are molecules made of?”

In this work I shall be concerned with *qualitative* descriptions of the electronic structure of molecules and only using detailed calculations “in the background” to provide illustrations but the large-scale analysis still has to be done to make sense of the structure of even quite small molecules.

1.2 What are Molecules Made Of?

Anyone with even a smattering of chemical experience can provide a list of possible answers to the question “what are molecules made of?” and these answers might be sorted “by size”:

- (1) Molecules are composed of functional groups and structural backbones.
- (2) Molecules are composed of atoms.

- (3) Molecules are composed of bonds, lone pairs and delocalised electron structures.
- (4) Molecules are composed of electrons and nuclei.

and all these answers are correct. Each of these answers is correct *for a particular way of thinking about molecules*. The question which we must address is:

What are the substructures of a molecule which are optimum for a meaningful description of their electronic structure?

In this context the first of the above answers can be discarded since it is the way that a chemist concerned with the practical problems of synthesis might break down the structure of a molecule in their minds. The last of the answers looks more like a description of the structure of a metal than that of a molecule; it is more a physicist's analysis than a chemist's and will also be discarded.

There are now two serious contenders for the method to use; are molecules made of atoms or are they made of bonds, lone pairs and other electronic structures? We might pause to think about what we mean by "made of"; we might mean "are constructed from" or, "can be made to emit" or "can be shown to contain". What is certainly true is that molecules can be constructed from atoms¹ and molecules may be broken up into atoms² whereas we cannot isolate (*e.g.*) a lone pair or a π -bond from a molecule and certainly cannot use such objects to make molecules. Colloquially we might say

Are molecules made of the subsystems like walls are made of bricks or like omelettes are made of eggs?

In fact, the real question is a little more precise than the one I have asked, what we really require is the answer to the question:

What substructures are the *electronic structures* of molecules made of? What is the best choice of electronic substructures in order to make sense of the structure and properties of molecules?

When posed in this way the choice seems easier but, as I shall try to show, the choice is never obvious and we shall always have to have *both* of the answers 2 and 3 in mind all the time. In fact, it will become clear that

¹With a great deal of difficulty, though.

²Again, not easily.

it is absolutely essential to keep these two points of view and the tension between them in mind all the time if we want to create a realistic qualitative theory of the electronic structure of molecules; a theory that can be made quantitative enough to be sure that we are on the right lines.

1.3 Interactions Between Atoms

If we take the point of view that molecules are made of atoms then we can think about what might happen when atoms approach one another; what are the processes which occur³ under these circumstances? First of all we need to think about what atoms actually *are* at the simplest possible level; let's say for the moment that an atom is just a (relatively) massive positively-charged nucleus surrounded by a cloud of (relatively) light negatively-charged electrons with the atom being overall electrically neutral (the charge on the nucleus—the atomic number—being the same as the number of surrounding electrons). What can happen to such structures when they are brought together close enough for them to be influenced by each other's distribution of electrical charges?

First of all we can treat one atom as stationary in the sense that we can think of the nucleus of one of the interacting atoms as being at a fixed point in space surrounded by its electrons as the other atom approaches. The electrons of this atom are, of course, in constant motion around the nucleus and are kept captive by the attraction between the (positively-charged) nucleus and their own negative charge. How will the approach of another, similar, system of charges affect the atom? There are, at least, two effects which come to mind immediately:

- (1) The target atom's electron distribution will be *polarised* by the approach of any charged body or rather the collection of charged bodies which is the approaching atom. The motions of the atom's electrons will be changed by the combination of attractions and repulsions between the charged particles in target atom and the approaching atom. Or to put it in more convenient language, the *distribution* of the target atom's electrons will be distorted. That is, the electron distribution around the atom will no longer be spherically symmetrical in the presence of another atom.⁴

³Or we might think of as occurring.

⁴Of course, the target atom will distort the distribution of the electrons on the approaching atom in a similar way.

- (2) Similarly, due to the electrostatic interactions between the two sets of particles of which the atoms are composed, the distribution of each atom's electrons may be changed in another way: the overall "size" of the electron distributions may change due to some of the electrons' moving closer to or further from their own nucleus as they "feel" the attractions and repulsions from the other atom. Each atom may get slightly bigger or smaller due to the presence of the other atom.

Naturally, these two effects do not happen *separately*; what must happen in practice is that the electron distributions interact with each other and distort with any expansion or contraction occurring *simultaneously* with any polarisation of the original distribution. But we can separate these two effects in our minds to try and understand each one individually.

Finally, as the two atoms approach closely, some of the electrons of both may be sufficiently attracted to both nuclei *simultaneously* to disrupt their original motions around their "own" nucleus completely and take up a completely new set of motions ("distribution") around *both* nuclei. When this happens, the two atoms are involved in a completely new set of circumstances; they are held together by these electrons which are attracted strongly to *both* nuclei—in a word they are *shared* between the two nuclei—and they hold the two nuclei together in a combined system which we recognise as a chemical bond.

Returning to the two answers to the question "what are molecules made of" we can now see the way in which the two answers 2 and 3 on page 5 are intertwined; we can easily say that our simple considerations could be interpreted in two ways:

- (1) The two *atoms* are joined by a chemical bond or
- (2) The electron distribution around the two *nuclei* has taken up a new structure; some of the electrons are distributed in a similar way around the nuclei but some electrons have changed their distribution radically.

Both descriptions are correct; the first is just a useful *name* for what has happened and the second is a mechanistic *explanation* of what *caused* the phenomenon. In this work we shall be mostly concerned with the second of these interpretations and, sooner or later, we shall have to decide what we mean by the term "explanation".

1.4 The Simplest examples: H₂ and LiH

1.4.1 The Hydrogen Molecule

Before starting to get a handle on a quantum-mechanical theory of these processes let's look at the simplest possible case: the hydrogen molecule. This is simply a look-ahead at some results which will be explained later but which enables us to see if we are even approximately on the right track. No attempt will be made yet to say how these results were obtained, they must be taken on trust for the moment.

The way that quantum-mechanical calculations are actually performed has some interesting advantages which we shall meet in due course, for the moment we simply note that it is actually possible using standard methods of quantum chemistry to perform calculations which approximately separate the two effects discussed in 2 and 3 on page 5 and see the effect of the mutual polarisations and expansions/contractions of the two atomic electron distributions separately.⁵ The table below gives the bond energy of the H₂ molecule as calculated allowing the two effects separately and together. For interest the experimental bond energy is given.

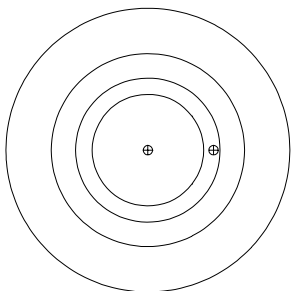
Type of Calculation	Calculated Bond Energy (kJ mol ⁻¹)
Unchanged Atomic Orbitals	190.86
“Size-Optimised Atomic Orbitals”	310.33 (change is 119.47)
“Polarised-only Atomic Orbitals”	229.53 (change is 38.67)
“Size-Optimised and Polarised AOs”	326.36 (change is 135.5)
Experimental Bond Energy	435.56

It is quite easy to see in this particular case that the effect of changes of size (contraction, in this case) of the electron distributions of the two atoms on the calculated bond energy is noticeably larger than the effect of their mutual polarisations. This fact is in line with the fact that the energy required to polarise the hydrogen atom is quite high. Obviously, the more polarisable the atom, the more it *will* be polarised in a molecular environment. It is also easy to see that the calculations do not satisfactorily reproduce the numerical value of the bond energy—more on this later.⁶

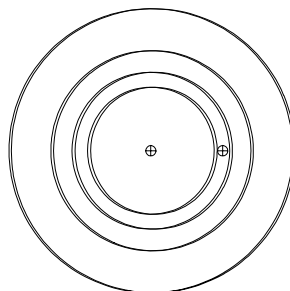
⁵For the experts, this is done by choice of orbital basis.

⁶Notice that the two effects (as calculated here) are not quite independent; the sum of the two “independent” changes is larger than the combined total change; the method does not succeed in completely separating the two effects, something else to look at later.

As the contour⁷ diagrams below illustrate, the *polarisation* of each H atom is a very slight shift of the contours in the direction of the other atom. In fact, the change in size (*contraction*) of each atom's electron distribution is too small to be seen on the scale of these contours; it is a very slight "pulling in" of the contours when shown on a much-enlarged scale. In the diagram the positions of the two hydrogen nuclei are given by the small crosses, so there are two diagrams of the *whole molecule* given below, showing the fact that the electron distribution of *each atom* overlaps both nuclei. So, the original electron distribution of the left-hand hydrogen atom is shown in the left-hand diagram together with the positions of both nuclei and the contracted, polarised distribution shown on the right-hand atom of the right-hand diagram. The two almost identical contours on the right-hand diagram are the contracted distribution and the contracted, polarised distribution. In the case of the electron in the hydrogen atom, which is very tightly-bound to its nucleus, there is nothing much to be seen.



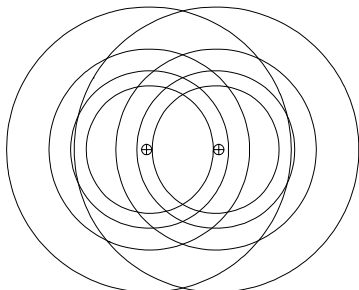
Atomic electron distribution
on left-hand atom



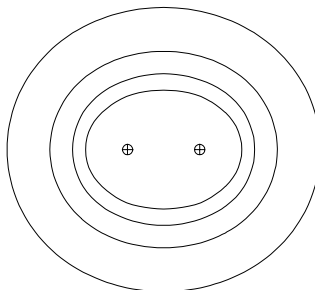
Contracted, Polarised distribution
on left-hand atom

Finally, contour diagrams of the electron distribution when the two contracted, polarised atomic distributions (left-hand diagram) are allowed to interact fully to form the molecule H_2 (on the right). Notice how the full interaction—when both electrons are attracted to both nuclei—is more compact than the original atomic distributions.

⁷See Appendix A at the end of this chapter for hints on how to interpret contour diagrams



Atomic electron distributions
of the two atoms superposed



Electronic distribution of
the Molecule

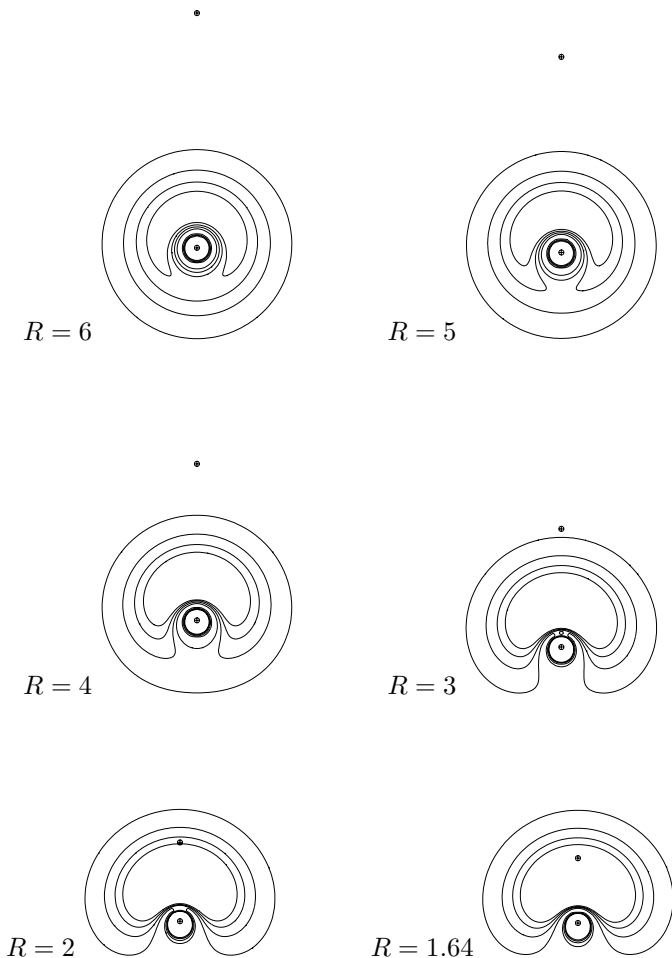
Overall, the results of these calculations are hardly definitive; the effects we predicted are present but scarcely spectacular.

1.4.2 *The Lithium Hydride Molecule*

The lithium hydride molecule is much more interesting in this context because it has two *different* atoms, the lithium atom having one of its electrons (the “outer” one) which is much less tightly bound to its nucleus than the electron of the hydrogen atom and so is much easier to move around.⁸ The effect of expansion or contraction of the atomic charge distributions is difficult to predict on the basis of simple ideas but, if the outer electron of the lithium atom is easier to remove from the atom or excite, it should also be easier to distort or polarise its distribution. Lets see what happens.

Below are very simple contour diagrams of the distribution of the outer ($2s$) electron of the lithium atom as it is approached by a hydrogen atom; only the position of the hydrogen *nucleus* is shown (vertically above the lithium). The hydrogen atom’s electron distribution—which is not visibly polarised on the scale of these diagrams—is omitted for clarity. The internuclear distances (R) are 6, 5, 4, 3, 2 and 1.64 (the experimental bond length) respectively.

⁸The energy required to remove the outer electron of a lithium atom is only 40% of the energy needed to remove the hydrogen atom’s electron and the energy required to excite the lithium $2s$ electron is also much less than that required to excite the hydrogen $1s$ electron.



In this case it is quite clear what is happening; as the hydrogen atom approaches, the polarisable outer electron distribution of the lithium atom is attracted to the approaching atom. At very large distances the lithium atom senses nothing and remains spherical but, as the hydrogen atom comes within the effective electrostatic range of the other atom:

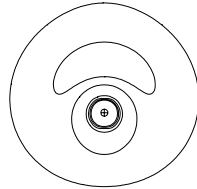
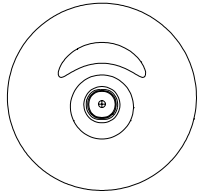
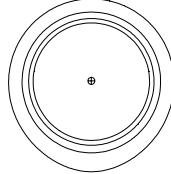
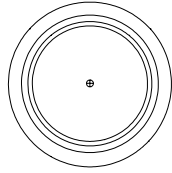
- The electron distribution is pulled towards that atom; the spherical appearance is progressively distorted and
- The electron distribution is concentrated more in the inter-atomic region; more contours appear in that region.

This polarised electron distribution is attracted to the hydrogen nucleus—and repelled by the hydrogen’s electron, of course; the net effect is attraction—and the (much less polarised) hydrogen atom electronic distribution also experiences net attraction to the lithium atom. At close enough approach, the overall effect is the same as in the hydrogen molecule:

When these two atoms approach each other closely enough the electron distributions of the outer electrons of the two atoms⁹ are completely disrupted by their changed environment and take up a new distribution around *both* nuclei which binds those nuclei together in a single chemical bond.

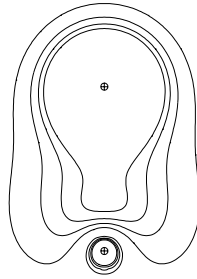
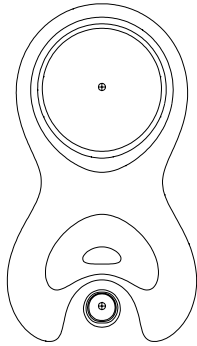
For completeness, the “molecular” electron distributions at the distances in the above diagrams are given below.

⁹The “outer” electron of the hydrogen atom is its only one, of course!



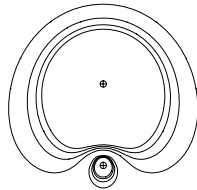
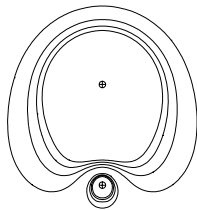
$R = 6$

$R = 5$



$R = 4$

$R = 3$



$R = 2$

$R = 1.64$

It is clear from these simple diagrams that there is little tendency for a molecule to form at all at the two largest distances; at $R = 5$ and $R = 6$. All that happens is that the *atomic* electron distributions are distorted by each other's presence. Only when the two atoms approach to a distance of $R = 4$ or less do we see marked changes in the electron distribution indicating something new happening. When the internuclear distance is reduced to around $R = 2$ or $R = 1.64$ is the electron distribution obviously that of a combined molecule; a single bond.

1.4.2.1 *What About the Other Li Electrons?*

In the above discussion we have said nothing at all about the “inner” two electrons of the lithium atom. These two electrons (the $1s^2$ shell) are very tightly held by their close proximity to the lithium nucleus (charge +3). They are *extremely* difficult to disturb; their distributions are not affected by the presence of an approaching hydrogen atom. In fact, their distribution is not appreciably affected by molecule formation.

1.4.2.2 *What About the Nuclear Repulsions?*

What has been said about the way the pairs of electrons in the hydrogen and lithium hydride molecules become re-arranged when the atoms approach one another is all very well and, although it is nice to see our predictions on page 6 verified, we cannot yet tell whether or not these changes are sufficient to hold the two nuclei together. This is because only those changes which might be thought to hold the nuclei together have been considered. The calculations illustrated by the diagrams were done by simply *fixing* the nuclei at the quoted distances and seeing how the electrons responded. What about those effects, if any, forcing the atoms apart? In other words, what about the fact that the two *nuclei* repel each other because they are both positively charged?

Will the re-arrangement of the electrons which have been described be sufficient to *overcome* this repulsive force? Unfortunately the answer is “sometimes it is and sometimes it isn't” depending on the individual case. Simple evidence for this is easily found by going to the stores in any chemistry laboratory and asking for (cylinders of) hydrogen and helium. In the one case—hydrogen—the cylinder will contain molecules and in the other—helium—one will find atoms. The stubborn refusal of helium atoms (and the other “noble” gases: neon, argon *etc.*) to form molecules is just

as much in need of explanation as the eagerness of hydrogen to bond with practically any atom. We shall have to look at this in detail later.

1.4.3 Comments on H_2 and LiH

How do our original comments on what might happen when atoms approach hold up in view of these results? Remember that we have not yet found out the theory and methods used in these calculations, that is for later. For the moment they are just presented as illustrations to be taken on trust.

In the case of the hydrogen molecule there is nothing much to see; two of the three distinct effects we thought might happen are hardly visible:

- The change in overall size of the atomic electron distributions is too small to see on the contour diagrams, although the calculated bond energies show that it is present. The detailed numerical results of the calculation show that this effect does occur; the atomic electron distribution does, in fact, contract on molecule formation.
- The polarisation of each atom's electron distribution by the other's presence *is* visible but it is a very small effect in the case of hydrogen
- However, on very close approach, the two atoms' electron distributions are disrupted and a new, molecular, electron distribution emerges corresponding to what we see experimentally; two hydrogen atoms are more stable as a molecule than as separate atoms.

The lithium hydride molecule presents a completely different picture. This time:

- The polarisation of the more loosely-bound outer electron's distribution is clearly visible in the diagrams, changing from the original atomic spherically-symmetric distribution to a very directional distribution with close approach of the hydrogen atom.
- The change in size of each atom is, however, again only to be detected by the change in bond energy being too small to notice on the contour diagrams.
- Just as in the case of H_2 , the electron distribution of the two atoms takes on a distinctly new, molecular, form at small internuclear distances.
- There is an "inner shell" of two $1s$ electrons on the lithium atom which is basically unchanged on molecule formation; these electrons are held so tightly by their "parent" nucleus that their distribution is scarcely affected by their new environment.

1.5 How to Proceed?

This very simple introductory chapter has raised many more questions than it has answered and has not touched on the major questions raised by the experimental facts of chemistry:

- What about *polyatomic* molecules? How are atomic electron distributions changed and combined when an atom is bonded to more than one other?
- Why does bonding *saturate*? Why does (*e.g.*) a carbon atom overwhelmingly form four bonds and not three or six?
- How is the *shape* of polyatomic molecules determined? The simple diatomics we have looked at have no choice about their shape.

These kinds of question are all capable of being given quantitative answers by the methods of quantum chemistry and, more important from the point of view being taken here, the answers to these questions can all be understood *qualitatively* using the techniques which will be developed.

What I have been concerned with here has been the most *basic* of all the methods we shall have to use to understand the electronic structure of molecules; the question raised on page 5:

Before we even to begin to think about the structure of a complex system like a molecule we have to use some experimental information to decide on the nature of the basic substructures within the molecule—what are molecules made of, what is the most fruitful breakdown of the overall structure into small structures? And, how do these substructures interact?

The examples of Section 1.4 provide some pointers:

- The hydrogen molecule is the simplest possible (chemically stable¹⁰) molecule and its electronic structure is such that *all* —*i.e.* both—its electrons having taken up a distribution around both nuclei to form a single chemical bond. There are *no* substructures in the hydrogen molecule; it can be seen as a *pair* of bonded atoms or as a *single* electron-pair bond according to point of view.
- Lithium hydride is more interesting. We have seen that the electronic structure of the molecule consists of two substructures:

¹⁰The one-electron molecular-ion H_2^+ does exist but it is not the sort of thing that one can get in a bottle.

- (1) The inner shell of the lithium atom (the two electrons in the $1s^2$ shell) which have basically the same distribution in the atom and in the molecule.
- (2) The two electrons involved in the chemical bond whose distribution (and energy) are completely different in the molecule from their separate atomic distributions.

So, to labour the point, the six-particle system which is the lithium hydride molecule (two nuclei and four electrons) can be seen to consist of two two-electron substructures which interact of course but whose basic structures are insensitive to changes in each-others' detailed structure.

The last point is the so-called "core-valence separation" and is the most obvious example of the more general point of view adopted here:

The electronic structure of molecules is composed of "environment insensitive" substructures. As we shall come to see later, the ones of interest are often just *pairs* of electrons (bonds, lone pairs) but may be larger groups (inner shells, conjugated π systems).

If we return to the analogy with the solar system we can see that:

Before we can calculate the details of the motions of the planets and their satellites, we have to know, among other things, how they are grouped together (how many moons has Jupiter?) and the fact that their orbits generally lie in a plane. Only then can we bring to bear the massive power of Newton's mechanics to predict their motions with enormous accuracy.

Likewise

Before we can compute the detailed distributions of the electrons we have to know (among other things) how the electrons are grouped, what relationships their distributions bear to the electron distributions in the separate atoms. Only then can we call on the big guns of Schrödinger's mechanics to calculate electron distributions and molecular shapes which can, in fact, be done with almost arbitrary accuracy.

So, the first thing to do is to see what we actually do know about the electronic structure of atoms and what we know about the ways in which atoms do combine to form molecules. This means another chapter.