

Third Edition

Symmetry and Structure

Readable Group Theory
for Chemists

Sidney F. A. Kettle

 WILEY



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Sidney F. A. Kettle

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and Pharmacy, University of East Anglia*



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West Sussex PO19 8SQ, England

Telephone (+44) 1243 779777

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Anniversary Logo Design: Richard J. Pacifico

Library of Congress Cataloging-in-Publication Data

Kettle, S. F. A. (Sidney Francis Alan)

Symmetry and structure : readable group theory for chemists / Sidney F. A.

Kettle. – 3rd ed.

p. cm.

ISBN 978-0-470-06039-1

1. Chemical structure. 2. Symmetry (Physics) 3. Group theory.

4. Chemical bonds. 5. Molecules. I. Title.

QD471.K47516 2007

541'.22015122–dc22

2007014664

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 9780470060391 HB

ISBN 9780470060407 PB

Typeset in 10/12pt Times by Aptara, New Delhi, India

Printed and bound in Great Britain by Antony Rome Ltd, Chippenham, Wiltshire

This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

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Preface to Third Edition

Although this third edition of 'Symmetry and Structure' has much in common with previous editions, there are major differences too. Most important is a new emphasis on the fact that irreducible representations characterize particular nodal patterns (or vice versa!). It is possible to draw pictures of these nodal patterns and so to give pictorial illustrations of irreducible representations. This is particularly useful for the simpler groups, where much of the group theory may be done pictorially. To obtain the maximum benefit from this approach, Chapters 2–4 contain a basic but reasonably complete overview of the application of group theory to chemistry (or, more accurately, the water molecule!). The major omission, of course, is that of degeneracy. The nodal pattern approach applies not only to the simple groups. Its use has enabled the inclusion of a chapter on electron spin, double groups and spin-orbit coupling. The inclusion of these has been facilitated by the addition of a chapter which includes the spherical group. Hopefully, the treatment of double groups is both readable and accurate. In general, the mathematical content of the book has been reduced, both in the text and in the Appendices. Although clearly there are limits, I have tried to make each chapter as independent as possible. This has led to some duplication of material – which may be no bad thing. By providing cross-references, the student can obtain a, somewhat, different approach to a difficult point, should the need arise. Above all, I have borne in mind the sub-title of the book, that the content should be readable, and with no loss of accuracy. If at some points the reader finds it fun too, that would be a bonus.

I am particularly grateful to Professors K. Gatterer (Graz) and E. Diana (Turin) for providing material which I have used and also for their comments on the text itself. All deficiencies which remain are, of course, my responsibility.

Sidney F.A. Kettle
Tuttington

1 Theories in conflict

1.1 Introduction

As its title says, this book is concerned with the symmetry and structure of molecules. Of these, the latter – both in the sense of the geometric and of the electronic structure of molecules – has long been of concern to chemists. We shall be interested in both these aspects and will adopt the viewpoint that the geometric structure of a molecule tells us something about its electronic structure. The connection between the two will be provided by the molecular symmetry, or rather its expression in what is called group theory. Ultimately, however, this book is concerned with the chemical consequences of molecular symmetry, the application of group theory to molecules, and these extend far beyond the problems of chemical bonding. Rather, the problem of chemical bonding will be used as a particularly convenient – and important – way of introducing the concepts of symmetry. The concepts revealed in this way can then be extended to other areas of chemistry. In an introductory text such as this there will be no attempt to cover all of the uses of symmetry in chemistry – an objective which it would be difficult to achieve in any text. Rather, the more important aspects will be detailed, but sometimes with more than a hint of the advanced. The aim will be to provide a cover of the basics of the subject sufficient to enable the reader to apply them in other areas. Further, this will be done in a readable, almost entirely non-mathematical manner. The take-home message is that the use of symmetry in chemistry is all about phase patterns: that is, about nodal planes akin to those that distinguish different atomic orbitals. But this is to come; in the present chapter we cover material that, hopefully, is familiar to the reader – explanations of why molecules have the shapes that are observed. The examples covered are chosen to be simple and mostly well known. But the final conclusions are surprising and lead us to query the validity of the simple models that we discuss. Rather than exploring these uncertainties, we will find more value in reversing the argument – and this reversal will be a recurrent theme throughout the book. It has already been mentioned. Start with the observed structure and use this to obtain information about the bonding. But first, the more traditional approach.

1.2 The ammonia molecule

The ammonia molecule provides a convenient starting point for our study and it will be used to see the problem of chemical bonding in a rather unusual perspective, one that leads to the approach indicated above – the attempt to infer molecular bonding *from* molecular

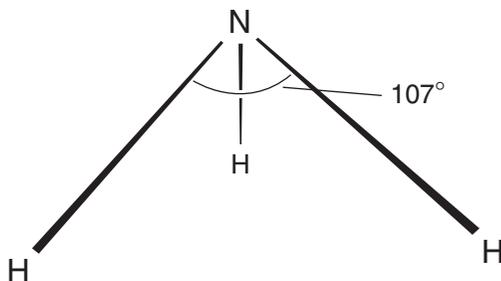


Figure 1.1 The ammonia molecule; the models in the text seek to explain the experimental bond angle

geometry (in contrast to the more common procedure of explaining molecular geometry in terms of chemical bonding). Several approaches to the bonding in the ammonia molecule will first be reviewed, approaches which have been in the chemical literature for many years. The reader may well not be familiar with all of them but he or she should not feel that they have to spend much time trying to master any new ones – our concern is with generalities, not details. However, references are given to enable the reader to explore any of the approaches in more detail, if they so wish.

1.2.1 *The atomic orbital model*

This model has an historic importance – it is the only description to be found in many pre-1955 texts.¹ Before looking at it, the facts. The ammonia molecule is pyramidal in shape; all three hydrogen atoms are equivalent, the HNH bond angle being 107° (Figure 1.1). Note the restriction that has implicitly been made: we will not attempt to explain bond lengths, only angles. The simplest, and oldest, explanation of the (angular) shape follows from the recognition that the ground state electronic configuration of an isolated nitrogen atom is $(1s)^2 (2s)^2 (2p)^3$, each of the 2p electrons occupying a different p orbital. Each of these 2p electrons may be paired with the electron present in the 1s orbital of a hydrogen atom by placing one hydrogen atom at one end of each 2p orbital so that each nitrogen 2p orbital overlaps with a hydrogen 1s orbital, giving a localized N–H bond. The result is an ammonia molecule which has the correct, pyramidal shape and which has all of three hydrogen atoms equivalently bonded to the nitrogen (Figure 1.2). However, the angle between any pair of 2p orbitals is 90° so that a bond angle of 90° is predicted by this model. Agreement with an experimental value of 107° is obtained by postulating the existence of electrostatic repulsion forces between the hydrogen atoms, each of which, it is assumed, carries a small residual charge. These repulsions cause the H atoms to move further apart – and so the bond angles increase. If, as seems probable, each N–H bond is slightly polar with each hydrogen carrying a small positive charge, this repulsion is nuclear–nuclear in origin. The consequent modification of the original bonding scheme as a result of this distortion of the bond angle from 90° is not usually considered.²

¹ See, for example, p. 65 of *Inorganic Chemistry*, by E. de Barry-Barnett and C.L. Wilson, Longman Green, London, 1953.

² The reader who wishes to perform this correction should make a note to do it after they have read Chapter 7, when they will be adequately equipped.

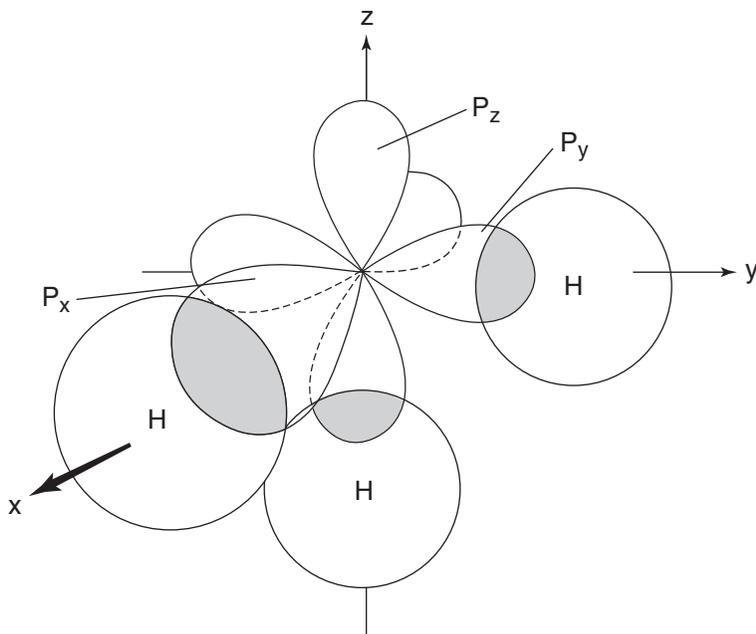


Figure 1.2 N—H bonding in NH_3 envisaged as resulting from the overlap of 2p orbitals of the nitrogen with 1s orbitals of the hydrogens. Because the three nitrogen 2p orbitals have their maximum amplitudes at 90° to each other, bond angles of this value are predicted. The overlap regions are shown shaded

1.2.2 The hybrid orbital model

This is detailed in many post-1955 texts.³ In this model an alternative description of the bonding in the ammonia molecule is obtained by hybridizing the valence shell orbitals of an isolated nitrogen atom, $2s$, $2p_x$, $2p_y$ and $2p_z$, to give four, equivalent, sp^3 hybrid orbitals pointing towards the corners of a regular tetrahedron. Because there are five electrons in the valence shell of the nitrogen atom, three of these hybrid orbitals may be regarded as containing one electron whilst the fourth is occupied by two electrons. As in the previous model, 1s electrons from three hydrogen atoms pair with the unpaired electrons on the nitrogen, now in hybrid orbitals, to give three localized bonds and a pyramidal ammonia molecule (Figure 1.3). Again, the three hydrogen atoms are equivalent but the bond angle is predicted to be 109.5° , the angle between the axes of a pair of sp^3 hybrid orbitals. This value is in closer agreement with experiment than that given by the previous model but again some correction is needed if the experimental value is to be reproduced. This time, the predicted bond angle is too big so a different source has to be found for the correction. It is usually made by invoking the effects of electron–electron repulsion. It is this electron–electron repulsion which forms the basis of a third model for ammonia and so the way that the ‘hybrid orbital’ model is modified to give agreement with experiment is contained in the description of

³ See, for example, p. 159 of *Valency and Molecular Structure* by E. Cartmell and G.W.A. Fowles, Butterworth, London, 1956.

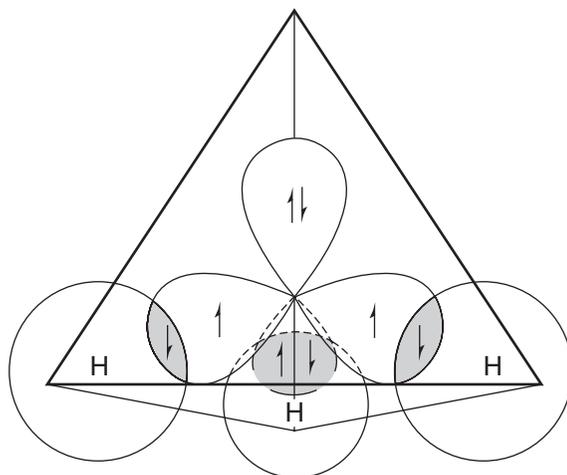


Figure 1.3 N—H bonding in NH_3 envisaged as resulting from the overlap of sp^3 hybrids of the nitrogen with $1s$ orbitals of the hydrogens. Because sp^3 hybrids (directed towards the corners of the tetrahedron shown) have their maximum amplitudes at 109° to each other, bond angles of this value are predicted. The overlap regions are shown shaded

the next model. The reader may well protest ‘what of the nuclear–nuclear repulsion of the previous model and why has it been ignored?’. Indeed this is a good question, but, equally, it is not to be overlooked that in the previous model we ignored electron–electron repulsion. We already detect an element of mutual inconsistency!

1.2.3 The electron-repulsion model

This is the model described in many current texts. The first two models considered above seek to explain the structure of the ammonia molecule in terms of the bonding interactions between the constituent atoms. The atoms adopt that arrangement which makes bonding a maximum. Repulsive forces, of one sort or another, were invoked only to get the predicted angles to agree with experiment.

In contrast, the present and the next model to be discussed explain the structure not in terms of bonding interactions (although these must exist to hold the atoms together) but by electron–electron repulsion. They recognize that electrons repel each other and regard the structure as being determined by the requirement that the inter-electron repulsion energies are minimized. The first of these models is originally due to Sidgwick and Powell, but has been subject to subsequent extensive elaboration and refinement, particularly by Nyholm and Gillespie. Over the years it has been the subject of both debate and further refinement.⁴

In the ammonia molecule there are four electron pairs involving the valence shell of the nitrogen atom. These are the three N—H bonding electron pairs and a non-bonding pair (in the first of the models discussed above these non-bonding electrons were placed in the $2s$

⁴ For a recent and readable review see ‘Models of molecular geometry’ by R.J. Gillespie and E.A. Robinson, *Chem. Soc. Rev. (London)* **34** (2005) 396. An idea of the development of the model over a decade can be gained by comparison with an earlier article by the same authors, ‘Electron domains and the VSEPR model of molecular geometry’, *Angew. Chem. Int. Ed.* **35** (1996) 495.

orbital of the nitrogen; in the second they were placed in an sp^3 hybrid orbital). Because electrons repel each other these four electron pairs would be expected to be as far apart as possible, consistent with still being bound to the nitrogen atom (three of the pairs are also individually bound to a hydrogen atom). It follows that the preferred orientation of these four electron pairs is that in which they point towards the corners of a regular tetrahedron. Remembering that three of the electron pairs are N—H bonding and that their orientation determines the positions of the hydrogen atoms, a HNH bond angle of 109.5° is predicted, the tetrahedral angle, the same as that given by the second model. Figure 1.3 also describes this model; the apical electron pair drawn there is expected to be a bit closer to the nitrogen nucleus than are the other three. It is thought-provoking to recognize that the same bond angle can be predicted either by including bonding interactions (the second model) or by ignoring them (this model)! Equally, by including electron–electron repulsion (this model) or by ignoring it (the second model)!

The refinement of the electron-repulsion model requires the recognition that there are two sorts of electron pairs, the three pairs involved in N—H bonding and a second sort, that which is non-bonding and located on the nitrogen atom. The electron pairs which comprise the N—H bonds are each subject to strong electrostatic attractions from two nuclei, the nitrogen nucleus and that of one of the hydrogen atoms. In contrast, the non-bonding electrons are strongly attracted by one nucleus only, that of nitrogen. It therefore seems reasonable to expect that the centre of gravity of the electron density in the N—H bonds will be located at a distance further away from the nitrogen nucleus than that of the lone pair electron density. The recognition of this difference at once leads to a refinement of the model. The accurate tetrahedral arrangement of four electron pairs resulted from the fact that, at that stage, all the electron pairs were precisely equivalent. In the absence of such equivalence a regular tetrahedral arrangement cannot be expected. It seems reasonable that the repulsive forces occurring between electron densities located in two N—H bonds will be less than the electrostatic repulsions between the non-bonding pair of electrons and a N—H bonding pair, simply because the distance between the centres of gravity of electron density will be greater in the former case. It would be expected that this difference in repulsion will lead the molecule to distort accordingly. The conclusion is that the HNH bond angle will be less than 109.5° . Although no quantitative prediction is possible with this simple model, the qualitative prediction is in accord with experiment – the bond angle is 107° . These same arguments, applied to the ‘hybrid orbital’ model (Section 1.2.2), also lead to qualitative agreement with experiment.

In more recent years, this, the Valence Shell Electron Repulsion (often abbreviated VSEPR) model, has become blended with another closely related model – the Ligand Close Packing (often abbreviated LCP) model. The word ‘ligand’ originates in transition metal chemistry, where it is used as the general name for groups attached to a (central, for simple molecules) metal atom. More loosely, it is used as a name for atoms or groups attached to a central one. The VSEPR model focuses attention on the central atom and the electron pair arrangement associated with it; almost as a book-keeping exercise, atoms or groups are attached to some of the electron pairs. The LCP model focuses attention on the ligands and explains geometry in terms of repulsions between them (any non-bonding electron pairs on the central atom are treated as if they were ligands). This approach clearly makes sense in those cases where a ligand is really bulky, *tert*-butyl for instance. An increased interest in bulky ligands (they change not only geometries but also reactivities) in recent years has no doubt encouraged interest in the LCP model. One aspect of the LCP model which is perhaps unexpected is

that it does not assume a fixed size for any ligand; the size of the ligand depends to some extent on the atom to which it is bonded. Apart from these remarks, we shall not develop the LCP model further; our interest is with the central atom and (ultimately) the symmetry of its surroundings, not repulsion between its components.⁵

1.2.4 *The electron-spin-repulsion model*

This is a little-used model,⁶ although it seems to be undergoing a minor resurgence.⁷ It differs from the preceding model principally in its recognition that electrons behave as individuals – and so repel each other as individuals – rather than as pairs. It is therefore more appropriate to consider eight electrons associated with the nitrogen atom, four with spin ‘up’ and four with spin ‘down’, than to think of there being four electron pairs (with no explicit mention of spin). In the case of eight individual electrons the preferred orientation (in which the electrons are as well separated spatially as possible) would be expected to be one in which the electrons are located at the corners of a cube. A result of detailed quantum mechanics is the recognition that an additional repulsion exists between electrons of like spin, compared with the repulsion between electrons of unlike spin. So, it would be anticipated that an electron of given spin would have as its nearest neighbours at the corners of the cube electrons of the opposite spin (the reader who would like the relationship between a cube and a tetrahedron described in more detail than given below should take a glance at Chapter 8 and, in particular, Figure 8.1). This means that in the cubic arrangement of electrons there would be four electrons with spin ‘up’ defining one tetrahedron and four with spin ‘down’ defining another. If lines are drawn from one corner of a cube across the face diagonals to other corners and this procedure continued, just four corners are reached. These four corners define a regular tetrahedron. Another regular tetrahedron is defined by the four corners which remain – see Figure 1.4. So far in this model all of the electrons have been associated with the nitrogen atom and we have really been thinking of N^{3-} , with eight valence shell electrons. It follows that when the hydrogen atoms are introduced they must be introduced as bare protons – so that an electrically neutral molecule results. These protons attract the eight electrons. The attraction between a proton and an electron does not depend upon whether the electron has its spin ‘up’ or ‘down’, although, of course, the extra repulsion between electrons of the same spin persists. The net result is that each proton attracts to its locality just one electron with spin ‘up’ and one with spin ‘down’. This attraction brings the two distinct tetrahedral arrangements of electrons into coincidence to give a single tetrahedral arrangement. The conclusion is that two electrons will be associated with each N–H bond and the remaining two will be non-bonding, just the same as for the previous model. Clearly, this model also predicts a bond angle of 109.5° , the tetrahedral value. It may be corrected in a manner similar to that described above for the electron pair model to give qualitative agreement with experiment. A word of caution. Although in this description there have been phrases such as ‘in the cubic arrangement of electrons’ this should not be thought of (for the isolated atom) as static; the atom is basically spherical, the electron

⁵ Those interested in exploring the LCP model and its relationship with the VSER will find a readable review by R.J. Gillespie and E.A. Robinson, *Chem. Soc. Rev. (London)* **34** (2005) 396.

⁶ It is described by J.W. Linnett in *The Electronic Structure of Molecules*, Methuen, London, 1964.

⁷ As part of a resurgence of valence bond theory.

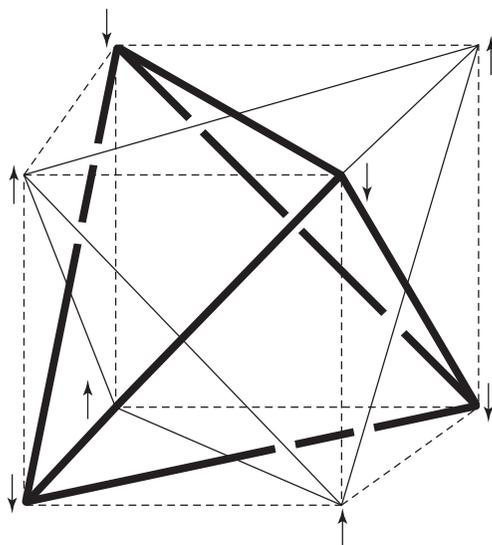


Figure 1.4 The two tetrahedra associated with a cube. Note the association that occurs in Linnett's model between these tetrahedra and the relative spins of the eight electrons placed at the corners of the cube. The thicker tetrahedron has spin 'down' at its corners; the thinner has spin 'up'

distribution smeared out. Rather it should be thought of as a slightly preferred arrangement, with the orientation of the cube totally undefined (and so totally free of constraints).

Although there is considerable overlap between the different models considered above, a survey of them does not lead to any definite conclusion regarding the relationship between the structure of and the bonding in the ammonia molecule. First, they are largely concerned with what is a relatively fine point – bond angles. They say nothing about the more important point (in terms of energy) of bond lengths. Second, all start with the supposition that only valence shell electrons need be considered but then diverge in their explanations. These explanations are not totally distinct but what one model regards as the dominant factor another assumes to be relatively small. The first two models, effectively, say that the geometry is determined by the requirement that bonding interactions be maximized whilst the last two say that it is the consequence of the requirement that non-bonding repulsive forces be minimized. One point that they have in common, however, is the fact that none of them leads to a prediction that the ammonia molecule should be planar.

1.2.5 Accurate calculations

In 1970 Clementi and his co-workers published the results of some very accurate calculations on the ammonia molecule.⁸ This is an old paper but the results remain valid – and it has the advantage of presenting the results in a way which provides insights relevant to the present chapter. Clementi and his colleagues were particularly interested in a study of the vibrational motion of the ammonia molecule in which it turns itself inside-out, like an umbrella in a high wind (Figure 1.5). Halfway between the two extremes of this umbrella motion the

⁸ A. Rauk, L.C. Allen and E. Clementi, *J. Chem. Phys.* **52** (1970) 4133.

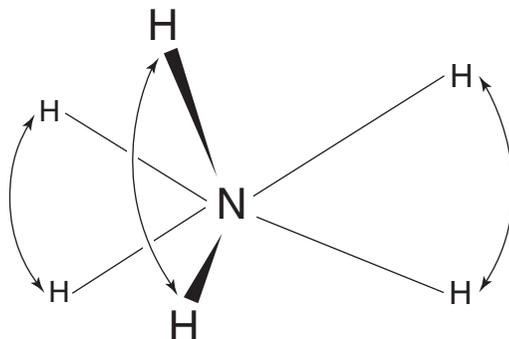


Figure 1.5 The 'umbrella' motion of the ammonia molecule. As the hydrogens move up and down together, so the nitrogen moves down and up, so that the centre of gravity of the molecule remains in the same place

ammonia molecule is planar. The energy barrier for the inversion is equal to the difference in total energy between the ammonia molecule in its normal, pyramidal, shape and the planar configuration. In order to obtain a theoretical value for this barrier, Clementi carried out rather detailed calculations for each geometry. The results obtained by Clementi were very surprising. They showed that the N—H bonding is greater in the planar molecule – there is a loss of N—H bonding energy of approximately $7.0 \times 10^2 \text{ kJ mol}^{-1}$ (167 kcal mol⁻¹) in going from the planar to the pyramidal geometry; this loss is accompanied by a slight lengthening of the N—H bond. Bonding favours a planar ammonia molecule. A comparison of the most stable pyramidal and most stable planar geometries shows that the electron–electron and nuclear–nuclear repulsion energies favour the pyramidal molecule over the planar by about $7.2 \times 10^2 \text{ kJ mol}^{-1}$ (172 kcal mol⁻¹). Repulsive forces favour a pyramidal molecule. Note the way that the bonding and repulsive energy changes between the two shapes almost exactly cancel each other. It is the slight dominance of the repulsive forces by 20 kJ mol^{-1} (5 kcal mol⁻¹) which leads to the equilibrium geometry of the ammonia molecule in its electronic ground state being pyramidal.

We are left with a most disturbing situation. There is no doubt that the strongest N—H bonding in the ammonia molecule is to be found when it is planar yet two of the simple models considered earlier in this chapter explained its geometry by the assumption that this bonding is a maximum in the pyramidal molecule! Similarly, the models based on electron–electron repulsion ignored both the fact that nuclear–nuclear repulsion is of comparable importance and the fact that their sum is almost exactly cancelled by changes in the bonding energy. This would not matter so much if there were some assurance that repulsive energies would outweigh the bonding in all molecules (molecular geometries could then reliably be explained using a repulsion-based argument). Unfortunately, no such general assurance can be given. This can be seen if the discussion of the ammonia molecule is extended to include some related species.

The molecules NH₃, PH₃, NH₂F, PH₂F, NHF₂, PHF₂, NF₃ and PF₃ all have similar, pyramidal, structures and would be treated similarly in all simple models. But calculations by Schmiedekamp and co-workers⁹ have shown that the first four owe their pyramidal

⁹ A. Schmiedekamp, S. Skaarup, P. Pulay and J.E. Boggs, *J. Chem. Phys.* **66** (1977) 5769.