MOLECULAR SHAPES

Theoretical Models of Inorganic Stereochemistry

JEREMY K. BURDETT

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Preface

Recent years have seen an explosion both in the number of new structural types that have been synthesized and in the number of structural studies undertaken by X-ray and neutron diffraction methods. Theoretical ideas to rationalize these new and exciting structural results are much in demand. The theoretical world is however at present divided as to how to meet this need. One group prefers to perform high-quality molecular orbital calculations on a limited series of molecular configurations and relies heavily on computer-generated numerical data. The other group uses molecular orbital results from much cruder molecular orbital methods, leans to a much smaller extent on exact numerology, and tries to find a symmetry or overlap explanation whenever possible. This second group has been led by the sterling efforts of Roald Hoffmann whose analogous treatment of the organic field a decade ago provided the impetus for a revolution in that area which brought theory and experiment much closer together.

Both approaches have their role to play. Good calculations are necessary to be able to reproduce detailed electronic properties of molecules such as photoelectron spectra, for example. But simple theories are of more interest to the average chemist. As L. S. Bartell has written, "By now chemists are fully accustomed to the gloomy rule of thumb that the more exact the quantum molecular calculation the more obscured by complexity is the physical interpretation and the less intelligible are the guidelines afforded to nonspecialists."[10] Similarly, in summarizing the inorganic chemist's view of molecular theories in 1970, J. W. Faller concluded: "It is the simple arguments, some naive, some well-founded on symmetry considerations, all drastic oversimplifications, that are most successful and practically useful" (p. 415 in Ref. 194).

Our aim in this book is to provide the reader with an account of various simple theoretical models of inorganic stereochemistry. There is no monopoly on ways to explain the same structural result, but some of the models are more generally applicable than others. The angular overlap model, for example, is widely used throughout this volume and provides a theoretical link between main group and transition metal stereochemistry, two areas that are often viewed separately. Our goal is to lead to an understanding of molecular structure rather than a cataloguing of numerical structural results in the sense of Hoffmann's comment that ". . . to understand an observable means being able to predict, albeit qualitatively, the result that a perfectly reliable calculation would yield for that observable."[93] However it should be constantly borne in mind when reading and using this book that our simple models are often drastic simplifications of the quantum mechanical "truth." In one sense they are just ways to collect together and organize experimental observations.

We hope to show in a general way how a small theoretical armory may be employed to tackle a range of structural problems. However the book is not a collection of explanations for each unusual structural quirk. (It could well be subtitled "The Structures of Simple Molecules.") The references similarly are not all-embracing. The majority of structural results quoted are to be found in Wells' elegant volume,[218] in Pearson's book,[163] or in the extremely valuable structural bibliographies provided by BIDICS[19] and the Chemical Society's Specialist Periodical Reports.[193] A comprehensive set of references covering experimental and theoretical studies on structural aspects of small main group molecules is to be found in Gimarc's recent book.[73]

One of the problems facing a writer of a book of this type is whether to include a discussion of the use of group theoretical methods in constructing molecular orbitals. This is done so well in Cotton's[40] little book that the motivation for including a substantial chapter in this volume was small. Although no significant discussion is included on this topic, the introductory chapters do include a collection of material basic to the study of molecular orbital theory.

The book has been read by several people at various stages of its gestation period. Particular thanks are due to T. A. Albright, R. S. Berry, and R. L. DeKock for their comments and criticisms, to Peri Gruber who drew the figures, and to Nancy Trombetta who typed the manuscript and made the many revisions and corrections with patience and good humor. To Professor Albright I am particularly indebted for his permission to reproduce the diagrams of Figure 13.8.

JEREMY K. BURDETT

Chicago, Illinois
May 1980

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A Note on Nomenclature

The following symbols and abbreviations appear in the text and are defined here for convenience:

A = main group atom
M = transition metal atom
H = hydride ligand (with σ orbital only)
Y = ligand in general (with π and σ orbitals)
X = halogen
L = ligand with π acceptor properties
B = shared electron pair on VSEPR scheme
E = unshared electron pair
HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital
ls = low spin
is = intermediate spin
hs = high spin
ϕ = atomic orbital
ψ = molecular orbital
Ψ = wavefunction describing electronic state
ϵ = interaction energy
$\Sigma(\sigma)$ = σ stabilization energy
$\Sigma(\pi)$ = π stabilization energy

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1 Introductory

Several simple theoretical results are described in this chapter that facilitate our understanding of the molecular orbital structures of molecules. In addition to these, we make extensive use of symmetry and group theoretical arguments, a powerful way to derive wavefunctions and classify energy levels in molecules.

1.1 Perturbation Theory

Of fundamental importance in the application of molecular orbital ideas to chemical problems is the use of perturbation theory to derive the wavefunctions and energies of a complex system from those of a much simpler one, where such information may be more readily obtained. We shall use the theory in many places throughout this book to view, for example, transition metal—or main group—ligand interaction or to understand how molecular orbitals mix when a molecule is distorted.

Consider a system described by a Hamiltonian $\mathscr{H}^{(0)}$ with a set of eigenvalues $E_m{}^{(0)}$ and eigenfunctions $\Psi_m{}^{(0)}$ such that

$$\mathscr{H}^{(0)}\Psi_m{}^{(0)} = E_m{}^{(0)}\Psi_m{}^{(0)} \tag{1.1}$$

Let us now disturb the system by applying a perturbation such that the perturbed system is described by the new Hamiltonian $\mathscr{H} = \mathscr{H}^{(0)} + \lambda\mathscr{H}'$ where λ is a parameter that allows us to gradually switch on the perturbation. Generally we may write for the new energies and wavefunctions

$$\begin{aligned} E' &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \\ \Psi' &= \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \cdots \end{aligned} \tag{1.2}$$

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where the $E^{(n)}$ and $\Psi^{(n)}$ are the nth order corrections to the energy and wavefunction, respectively. For the perturbed system the Schrödinger equation becomes for the mth state

$$\begin{multline}[\mathcal{H}^{(0)} + \lambda\mathcal{H}' - (E^{(0)} + \lambda E_m^{(1)} + \lambda^2 E_m^{(2)} \\ + \cdots)][\Psi_m^{(0)} + \lambda\Psi_m^{(1)} + \lambda^2\Psi_m^{(2)}] = 0 \quad (1.3)\end{multline}$$

If this is valid for all values of λ, then the functions multiplying each power of λ must each individually be zero in Equation 1.3. In first order (terms in λ),

$$(\mathcal{H}^{(0)} - E_m^{(0)})\Psi_m^{(1)} + (\mathcal{H}' - E_m^{(1)})\Psi_m^{(0)} = 0 \qquad (1.4)$$

If the perturbed wavefunction is approximated as an expansion of the unperturbed wavefunctions (Equation 1.5),

$$\Psi_m^{(1)} = \sum_n c_n^{(1)}\Psi_n^{(0)} \qquad (1.5)$$

then

$$\sum_n c_n^{(1)}(\mathcal{H}^{(0)} - E_m^{(0)})\Psi_m^{(0)} + (\mathcal{H}' - E_m^{(1)})\Psi_m^{(0)} = 0 \qquad (1.6)$$

In Equation 1.5* the $\Psi_n^{(0)}$ are orthonormal, that is,

$$\int \Psi_n^{(0)}\Psi_{n'}^{(0)}\,d\tau = \delta_{nn'} \qquad (1.7)$$

and

$$\int \Psi_n^{(0)}\mathcal{H}^{(0)}\Psi_{n'}^{(0)}\,d\tau = \delta_{nn'}E_{nn'}^{(0)} \qquad (1.8)$$

So premultiplying Equation 1.6 by $\Psi_m^{(0)}$ and integrating gives the first-order correction to the energy,

$$E_m^{(1)} = \int \Psi_m^{(0)}\mathcal{H}'\Psi_m^{(0)}\,d\tau \qquad (1.9)$$

In applying the results to a real chemical problem we may choose the value of the dummy parameter λ to be equal to unity such that $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}'$ and $E' = E^{(0)} + E^{(1)} + \cdots$. The first-order correction to the wavefunction is simply obtained by premultiplying Equation 1.6 by all other unperturbed wavefunctions $\Psi_n^{(0)}$ except $\Psi_m^{(0)}$ and integrating such that

---

* We shall always assume that our Ψ, ψ, or ϕ may be written as real functions and so shall not formally include the complex conjugate in such integrals.

$$\Psi_m^{(1)} = \sum_n{}' \frac{\int \Psi_m^{(0)}\mathcal{H}'\Psi_n^{(0)}\,d\tau}{\Delta E_{mn}} \cdot \Psi_n^{(0)} \tag{1.10}$$

where the prime indicates that $n = m$ is excluded from the summation and $\Delta E_{mn} = E_m^{(0)} - E_n^{(0)}$.

The second-order correction to the energy (Equation 1.11) is obtained via extraction of terms from Equation 1.3 containing λ^2:

$$(\mathcal{H}^{(0)} - E_m^{(0)})\Psi_m^{(2)} + (\mathcal{H}' - E_m^{(1)})\Psi_m^{(1)} - E_m^{(2)}\Psi_m^{(0)} = 0 \tag{1.11}$$

Expanding $\Psi_m^{(2)}$ as above,

$$\Psi_m^{(2)} = \sum_n c_n^{(2)}\Psi_n^{(0)} \tag{1.12}$$

and substituting into Equation 1.5 gives

$$\sum_n [c_n^{(2)}(\mathcal{H}^{(0)} - E_m^{(0)})\Psi_n^{(0)} + c_n^{(1)}(\mathcal{H}' - E_m^{(1)})\Psi_n^{(0)}] - E_m^{(2)}\Psi_m^{(0)} = 0 \tag{1.13}$$

Premultiplying by $\Psi_m^{(0)}$ and integrating as before gives

$$\sum_n{}' c_n^{(1)} \int \Psi_m^{(0)}\mathcal{H}'\Psi_n^{(0)}\,d\tau - E_m^{(2)} = 0 \tag{1.14}$$

which on substitution for $c_m^{(0)}$ gives

$$E_m^{(2)} = \sum_n{}' \frac{(\int \Psi_m^{(0)}\mathcal{H}'\Psi_n^{(0)}\,d\tau)^2}{\Delta E_{mn}} \tag{1.15}$$

Since the numerator is always positive, perturbation by states higher in energy than m leads to a negative contribution to the second-order energy, and perturbation by states lower in energy than m leads to a positive contribution. We use this result extensively in the discussion in this book. Higher-order perturbation results are obtained in a similar fashion. Sometimes we use these results as they stand, namely, to view the mixing of electronic states Ψ as a result of a perturbation. More often we are interested in the mixing of atomic (ϕ) or molecular (ψ) orbitals as the result of a perturbation, the results of which are approachable by exactly analogous mathematics by simply replacing Ψ by ψ or ϕ.

An alternative way exists of obtaining these results which has the advantage of revealing what is neglected in our analysis above and also of removing the assumption that the perturbation is small. Manipulation of the wave equation (see Ref. 144 for details) leads to a secular determinant (Equation 1.16),

$$\begin{vmatrix} H_{11}' - (E - E_1^{(0)}) & H_{12}' \ldots \\ H_{21}' & H_{22}' - (E - E_2^{(0)}) \ldots \\ \vdots & \vdots \end{vmatrix} = 0 \qquad (1.16)$$

which describes how the states or orbitals interact with each other when a perturbation $\mathcal{H}'$ is applied to the system; H_{ij}' is the integral $\int \psi_i \mathcal{H}' \psi_j \, d\tau$, and the roots of the determinant give the energy shifts $E_i^{(0)} - E_i$ of each level i that result. As a first approximation to E_m (for example) we can neglect all the elements in this determinant except H_{mm}', in which case $E_m = E_m^{(0)} + H_{mm}'$, a result identical to the first-order correction of Equation 1.9. By neglecting all elements of the determinant that do not lie in the mth row or mth column, we arrive at the second-order result of Equation 1.15. Inclusion of more elements of the secular determinant leads to the results of higher-order perturbation theory. In the following chapters we use both the secular determinant approach to calculate new energy levels as the result of a perturbation and also the results of second-order perturbation theory.

1.2 Overlap Integrals between Atomic Orbitals

To begin we consider some of the simple results of the solution of the Schrödinger Wave Equation for atoms. In particular we focus on the form of the wavefunctions and, as we are interested in chemical bonding, the ways of expressing the overlap integral between two orbitals on different atoms located in a specific geometric orientation with respect to each other.

Solution of the Schrödinger wave equation for a single electron, charge $-e$, and reduced mass μ moving in the potential produced by a nucleus of charge $+Ze$ leads to a series of eigenvalues and eigenvectors (Equation 1.17) defined by the three quantum numbers n, l, and m:

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}$$

$$\begin{aligned}\psi_{nlm} &= R_{nl}(r)\, Y_{lm}(\theta, \phi) \qquad (1.17)\\ &= R_{nl}(r)\Theta_{lm}(\theta)\, \Phi_m(\phi)\end{aligned}$$

The variables r, θ, and ϕ are the conventional polar coordinates. The Y_{lm} are spherical harmonics, $R_{nl}(r)$ contains the associated Laguerre functions, and the exact analytic form of Equation 1.17 is readily written down. Note that the energy of the orbital, defined by n, l, and m quantum numbers, is independent of l and m and is determined by the value (in nonrelativistic theory at least) of n only. Thus $3s$ ($nl = 30$), $3p$($nl = 31$), and $3d$($nl = 32$) are equienergetic. $\Phi(\phi)$ is given by Equation 1.18:

$$\Phi_m = N\, e^{im\phi} \qquad (1.18)$$

$N = 1/\sqrt{2\pi}$ is a normalization factor. To avoid the use of complex numbers, new functions are defined whenever $m \neq 0$. Thus

$$\begin{aligned} p_z\ \Phi_z &= \Phi_0 = N \qquad (m = 0)\\ p_x\ \Phi_x &= \frac{N}{\sqrt{2}}[\Phi_1 + \Phi_{-1}] = N\cos\phi \\ p_y\ \Phi_y &= \frac{Ni}{\sqrt{2}}[\Phi_1 - \Phi_{-1}] = N\sin\phi \end{aligned} \left.\vphantom{\frac{N}{\sqrt{2}}\frac{N}{\sqrt{2}}}\right\}(m = \pm 1) \qquad (1.19)$$

and their complete angular dependence is $\cos\theta$, $\sin\theta\cos\phi$, and $\sin\theta\sin\phi$, respectively.

For polyelectron atoms the Schrödinger wave equation becomes a many-body problem and cannot be solved exactly. Approximate solutions may be obtained by means which are referred to later. The most important result is that the wavefunctions take a similar form as before (Equation 1.20),

$$\psi_{nlm} = R'_{nl}(r)\, Y_{lm}(\theta, \phi) \qquad (1.20)$$

but with the vital difference that $R'_{nl}(r)$ is not a simple analytic function and cannot be obtained exactly. The $Y_{lm}(\theta, \phi)$ are the same spherical harmonics as before and are of course readily determined. However for single-electron and polyelectronic atoms the overlap integral between two orbitals on different atoms may be written in a simple fashion, Equation 1.21, as a product of radial and angular terms:

$$S_{ab} = S_{\lambda}(r)\,F(\theta, \phi, \lambda) \tag{1.21}$$

$S_{\lambda}(r)$ depends upon the distance between the two atomic centers, the nature of the atoms a and b (i.e., whether Cd, S, or Na, for example), and the n and l values of both orbitals. It is also dependent upon whether the overlap has local $\lambda = \sigma$, π, or δ symmetry. The angular term $F(\theta, \phi, \lambda)$ is a simple function of the angular polar coordinates of one atom relative to another, different functions being found for different values of λ. For example in Figure 1.1*a* the overlap integral between a p_z orbital on one atom and a σ type orbital on another is simply given by

$$S = S_{\sigma} \cos\theta \tag{1.22}$$

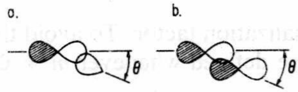

Figure 1.1 Overlap integrals between orbitals on two different atoms.

where S_{σ} contains all the radially dependent parts of the overlap integral and $\cos\theta$ all the angular dependence. Often for ease of calculation we need the overlap integral between two orbitals which are defined by a set of Cartesian axes (Figure 1.1*b*). In general the result is given by a sum of terms (Equation 1.23):

$$S = \sum_{\lambda=\sigma,\pi,\delta} S_{\lambda} F(\theta, \phi, \lambda) \tag{1.23}$$

In this particular example the overlap integral is simple $S = \sin^2\theta\, S_{\pi} - \cos^2\theta\, S_{\sigma}$. As will be seen on many occasions in this book, knowledge of the *angular* dependence only of the overlap integrals, which is the same irrespective of the chemical nature of a and b and the ab distance, is invaluable when looking at molecular structure. Tables 1.1 and 1.2 give values of the angular part of the overlap integrals between pairs of orbitals after the styles of Equations 1.21 (Figure 1.1*a*) and 1.23 (Figure 1.1*b*), respectively. Clearly the values in Table 1.1 are derived from those in Table 1.2 by a simple geometric transformation.

Table 1.1 Some Useful Overlap Integrals Between Central-Atom *s, p.* and *d* Orbitals and Ligand σ and π Orbitals[a,b]

$S(s,\sigma) = S_\sigma$

$S(s,\pi) = 0$

$S(z,\sigma) = HS_\sigma$

$S(z,\pi_\parallel) = IS_\pi$

$S(z,\pi_\perp) = 0$

$S(z^2,\sigma) = \frac{1}{2}(3H^2 - 1)S_\sigma$

$S(x^2 - y^2,\sigma) = \sqrt{3}/2(F^2 - G^2)S_\sigma$

$S(xy,\sigma) = \sqrt{3}FGS_\sigma$

$S(xz,\sigma) = \sqrt{3}FHS_\sigma$

$S(yz,\sigma) = \sqrt{3}GHS_\sigma$

$S(z^2,\pi_\parallel)$[c] $= \sqrt{3}HIS_\pi$

$S(z^2,\pi_\perp) = 0$

$S(x^2 - y^2,\pi_\parallel) = -HIS_\pi$

$S(x^2 - y^2,\pi_\perp) = 0$

$S(xy,\pi_\parallel) = 0$

$S(xy,\pi_\perp) = IS_\pi$

$S(xz,\pi_\parallel) = (I^2 - H^2)S_\pi$

$S(xz,\pi_\perp) = 0$

$S(yz,\pi_\parallel) = 0$

$S(yz,\pi_\perp) = HS_\pi$

$F = \sin\theta\cos\phi$

$G = \sin\theta\sin\phi$

$H = \cos\theta$

$I = \sin\theta$

---

[a] $\pi_\parallel$ is a ligand π orbital whose axis lies in a plane containing the *z*-axis and the ligand; $\pi_\perp$ is a ligand π orbital with an axis perpendicular to this plane.

[b] For p_z, d_{z^2}, f_{xyz}, etc. we use z, z^2, xyz, etc.

[c] Ligand lies in *xz* plane. For more general cases, manipulation of Table 1.2 is needed.

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