THE INTERNATIONAL ENCYCLOPEDIA OF PHYSICAL CHEMISTRY AND CHEMICAL PHYSICS

THE ELECTRONIC STRUCTURE OF MOLECULES: THEORY AND APPLICATION TO INORGANIC MOLECULES

BY

G. DOGGETT

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INTRODUCTION

THE International Encyclopedia of Physical Chemistry and Chemical Physics is a comprehensive and modern account of all aspects of the domain of science between chemistry and physics, and is written primarily for the graduate and research worker. The Editors-in-Chief, Professor D. D. ELEY, Professor J. E. MAYER and Professor F. C. TOMPKINS, have grouped the subject matter in some twenty groups (General Topics), each having its own editor. The complete work consists of about one hundred volumes, each volume being restricted to around two hundred pages and having a large measure of independence. Particular importance has been given to the exposition of the fundamental bases of each topic and to the development of the theoretical aspects; experimental details of an essentially practical nature are not emphasized although the theoretical background of techniques and procedures is fully developed.

The Encyclopedia is written throughout in English and the recommendations of the International Union of Pure and Applied Chemistry on notation and cognate matters in physical chemistry are adopted. Abbreviations for names of journals are in accordance with *The World List of Scientific Periodicals.*

PREFACE

THE aim of this book is to provide Chemistry students in their final year, or first year of postgraduate study, with a reasonably detailed account of the methods used for investigating the electronic structure of inorganic molecules and ions. The exposition has been kept as straightforward as possible so that the student can clearly discern the principles underlying the various model calculations. This approach has necessitated a lengthy introductory chapter on basic methods; but without this it is difficult for a beginner to develop an objective view of the problems inherent in a molecular structure calculation.

It is unfortunate, perhaps, that, in the space available, it has not been possible to say anything, for example, about the magnetic properties of transition metal ion complexes, or relevant aspects of the solid state—just to mention two omissions. Deficiencies such as these are unavoidable, unless the text is expanded considerably. In any case, my main concern has been to focus attention on the basic problems of determining the electronic structure of isolated molecules: the extra problems involved when the molecules are subjected to additional perturbations arising from external electric or magnetic fields are immense, and do not really fall within the confines of this section of the Encyclopedia.

This book was written while I was on the staff of the Chemistry Department, University of Glasgow, and I am indebted to my former colleagues, Dr. B. C. Webster and Dr. R. V. Emanuel, and research students for many stimulating discussions on various aspects of the manuscript. I would also like to thank Dr. T. Thirunamachandran for a critical reading of the manuscript, and my wife for her forbearance during the whole course of the writing and typing of the manuscript.

Glasgow, May 1970 G. DOGGETT

UNITS AND NOTATION

Lengths are given in nanometres (nm):

$$1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{ Å}.$$

$$1 \text{ a.u.} = a_0 = \frac{\epsilon_0 h^2}{\pi m e^2} = 0{\cdot}05292 \text{ nm} = 0{\cdot}5292 \text{ Å}.$$

($\epsilon_0 = 8{\cdot}854 \times 10^{-12} \text{ Fm}^{-1}$, the permittivity of free space.)

Energies are given in either atomic units (a.u.) or attojoules (aJ):

$$1 \text{ a.u.} = \frac{e^2}{4\pi\epsilon_0 a_0} = 4{\cdot}359 \text{ aJ} = 27{\cdot}21 \text{ eV}.$$

$$1 \text{ aJ} = 10^{-18} \text{ J} = 6{\cdot}242 \text{ eV} = 5{\cdot}035 \times 10^4 \text{ cm}^{-1}.$$

Dipole moments are given in Debyes:

$$1 \text{ D} = 10^{-18} \text{ e.s.u. cm} = 0{\cdot}3336 \times 10^{-29} \text{ Cm}.$$

All operators are represented by upper- or lower-case italic letters with a circumflex accent: for example, $\hat{H}$ or $\hat{s}_z(m)$.

$$\sum_{i,j}{}' A_{ij}$$

indicates summation over i and j, excluding the terms with $i = j$;

$$\sum_{j}{}' A_{ji}$$

indicates summation over j, excluding the term with $j = i$.

A superscript * indicates the complex conjugate.

Matrices are denoted by bold roman letters: for example, $\mathbf{S}$. The ijth element of $\mathbf{S}$ is denoted by either $(\mathbf{S})_{ij}$ or S_{ij}. The transpose of $\mathbf{S}$ is denoted by $\mathbf{S}'$, where $(\mathbf{S}')_{ij} = (\mathbf{S})_{ji}$. The adjoint of $\mathbf{S}$ is denoted by $\mathbf{S}^+$, where $(\mathbf{S}^+)_{ij} = (\mathbf{S}^*)_{ji}$. The trace of $\mathbf{S}$ is denoted by tr $\mathbf{S}$, and is given by the sum of the diagonal elements of $\mathbf{S}$ ($\mathbf{S}$ assumed square).

$\hat{P}$ is an operator which permutes electron labels.

The collection of symmetry operations associated with a general molecular point group is denoted by G.

$D_\Gamma(\hat{R})_{ji}$ is the jith element of the matrix representing the symmetry operation $\hat{R}$ in the irreducible representation Γ.

$\chi_\Gamma(\hat{R})$ is the character associated with the symmetry operation $\hat{R}$ in the irreducible representation Γ.

The following convention is adopted for displaying atomic orbitals in the figures representing electron-pairing schemes for molecular electronic structure:

s atomic orbitals are indicated by a single circular lobe;
p atomic orbitals are indicated by two (non-touching) circular lobes;
d atomic orbitals are indicated by four (non-touching) egg-shaped lobes (t_{2g} variety);
hybrid atomic orbitals are indicated by pear-shaped lobes.

This convention is necessary only for displaying the types of atomic orbital involved in the bonding, and the size of the lobes is not indicative of the spatial extension of the atomic orbitals.

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CHAPTER 1

ORBITAL THEORIES OF ELECTRONIC STRUCTURE

1.1. Introduction

A detailed understanding of the electronic structure of many-electron atoms and molecules still remains one of the basic problems in the application of wave mechanics to systems of chemical interest: this situation arises because the Schrödinger equation can be solved exactly only for one-electron atoms. Thus, in general, it is necessary to find approximate wave functions which simulate the exact wave function as well as possible. As described in Vol. 1 this usually means incorporating linear and non-linear parameters into the approximate wave function, and then applying the variation theorem to determine their optimum values. This technique has been used with great success in the study of some two-electron systems.

Pekeris[1] has calculated the binding energy of He more accurately than the experimentally determined value; while Kołos and Wolniewicz[2] have calculated the dissociation energy of H_2 to within the limits of error of the experimental value (see Herzberg, Bibliography). The numbers of variationally determined parameters in these calculations were 1078 and 55, respectively; a factor which precludes any generalization of these particular methods to molecules of chemical interest. Thus, rather than trying to calculate the binding energy of a transition metal ion complex which, in any case, may be smaller than the errors inherent in the calculation, it is more profitable to calculate changes in selected molecular properties within a series of closely related molecules. Any errors arising from the basic assumptions, or approximations, should then remain constant, so allowing the trend of a particular property to attain some meaning. An example of this approach is in the study of a particular band, or bands, in the electronic absorption spectrum of an octahedrally coordinated transition metal ion for different choices of ligand.

For very large molecules, the possibility of performing non-empirical wave mechanical calculations is quite remote, and further approximations are inevitably invoked. For example, it is usual to separate the electrons into groups: the valence electrons are considered in one group, while all the remaining electrons provide a non-polarizable core—just as σ-electrons do in π-electron theories of conjugated hydrocarbons. This separation is often necessary for making calculations tractable, and it is not a consequence of a particular symmetry requirement. In most cases, though, it represents a

reasonable approximation as many properties of chemical interest reflect changes in the distribution of the valence electrons. However, the core–valence electron separation requires handling carefully: particularly when the molecular wave function explicitly involves the valence electrons alone. Even though most experimental situations are dominated by changes within the group of valence electrons, there are some interesting cases where the effects of valence and core electrons cannot be separated completely: as found, for example, in the Mössbauer effect, X-ray emission spectra, contact spin coupling, and in understanding the finer details of nuclear quadrupole resonance spectroscopy.

Further simplifications can often be made for molecules possessing a high degree of symmetry. For example, an extensive understanding of the chemistry of planar unsaturated hydrocarbons has been achieved through the assumption of σ–π separability. Although the validity of this basic assumption is now in doubt, its use has undeniably correlated a large amount of experimental data (see Vol. 2).

As far as non-linear and non-planar inorganic molecules are concerned, and these include the highly symmetrical octahedral XY_6 and tetrahedral XY_4 molecules, it is not formally possible to effect a σ–π separation: nevertheless, it is often very useful to assume that the electronic structure of these symmetrical molecules can be discussed in terms of σ and π contributions to the overall bonding. In this context, of course, it is strictly only meaningful to use the terms σ and π when discussing the ligand–central atom interactions within a chosen bond: for it is only then that the cylindrical symmetry permits orbitals to be classified as either σ or π type.

It has so far been tacitly assumed that the properties of a particular molecule are adequately described in terms of the various electrons moving with respect to a fixed nuclear framework; that is, the electronic and nuclear motions have been separated through use of the Born–Oppenheimer[3] approximation, a preliminary discussion of which has already been given in Vol. 1. The Born–Oppenheimer approximation may not always be applicable and, when this is so, the consequences are of considerable interest. For this reason it is important to examine the assumptions implicit in the approximation, and to develop the necessary analysis in some detail.

1.2. The separation of electronic and nuclear motions

In Vol. 1 it was shown how the use of the Born–Oppenheimer approximation enables each bound state of a molecule to be represented by a product wave function of the form

$$\Phi_m^k = \tilde{\Psi}_m(\mathbf{r}; \mathbf{R}, \mathbf{s})\Lambda_m^k(\mathbf{R}). \tag{1.1}$$

r, **R**, **s** represent the complete sets of electron, nuclear and electron spin coordinates, respectively; and m, k label different electronic and nuclear wave functions, respectively. Thus for each electronic state $\tilde{\Psi}_m$ there is a set of nuclear wave functions Λ_m^k ($k = 1, 2 \ldots$) describing the vibrational and rotational states of the molecule.

The total spinless molecular Hamiltonian, $\hat{\mathscr{H}}$, is given by

$$\hat{\mathscr{H}} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,\alpha}\frac{Z_\alpha}{r_{\alpha i}} + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \frac{1}{2}\sum_\alpha \frac{m}{M_\alpha}\nabla_\alpha^2 \qquad (1.2)$$

where i, j label electrons and α, β label nuclei. The form of (1.2) implies energy is measured in units of $e^2/(4\pi\epsilon_0 a_0)$ (Hartrees), where a_0 is the atomic unit of length ($a_0 = \epsilon_0 h^2/\pi m e^2 = 1$ Bohr).

$\tilde{\Psi}_m$ is assumed to be a solution of the electronic Schrödinger equation

$$\hat{H}\tilde{\Psi}_m \equiv \left(-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,\alpha}\frac{Z_\alpha}{r_{\alpha i}} + \sum_{i<j}\frac{1}{r_{ij}}\right)\tilde{\Psi}_m = E_m(\mathbf{R})\tilde{\Psi}_m \qquad (1.3)$$

in which the nuclei are held in the fixed configuration **R**. The nuclear coordinates therefore appear as parameters in the electronic wave function, merely defining the nuclear configuration. For present purposes, $E_m(\mathbf{R})$ is assumed to be non-degenerate; thereby enabling $\tilde{\Psi}_m$ to be chosen real without any loss of generality.

The equation determining Λ_m^k is found by straightforward application of the variation theorem using (1.1) and (1.2):

$$\delta\int\int \Phi_m^k(\hat{\mathscr{H}} - \varepsilon_m^k)\Phi_m^k \,\mathrm{d}\tau\,\mathrm{d}\mathbf{R} = 0, \qquad (1.4)$$

where $\mathrm{d}\tau = \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{s} = \mathrm{d}\mathbf{r}_1\,\mathrm{d}s_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}s_2 \ldots = \mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1\,\mathrm{d}s_1\,\mathrm{d}x_2 \ldots$. Substitution of (1.1) and (1.2) in (1.4) then gives

$$\int\int \tilde{\Psi}_m \delta\Lambda_m^k \left[\hat{H} + \frac{1}{2}\sum_\alpha\left(-\frac{m}{M_\alpha}\right)\nabla_\alpha^2 + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \varepsilon_m^k\right]\tilde{\Psi}_m\Lambda_m^k \,\mathrm{d}\tau\,\mathrm{d}\mathbf{R} = 0$$

which, after using (1.3) and integrating over the electronic and spin coordinates, becomes

$$\int \delta\Lambda_m^k \left[E_m(\mathbf{R}) + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \frac{1}{2}\sum_\alpha\left(-\frac{m}{M_\alpha}\right)\int \tilde{\Psi}_m\nabla_\alpha^2\tilde{\Psi}_m \,\mathrm{d}\tau + \frac{1}{2}\sum_\alpha\left(-\frac{m}{M_\alpha}\right)\nabla_\alpha^2 - \varepsilon_m^k\right]\Lambda_m^k \,\mathrm{d}\mathbf{R} = 0, \qquad (1.5)$$

where the term involving the integral $\int \Psi_m\nabla_\alpha\Psi_m \,\mathrm{d}\tau$ vanishes since

$$\nabla_\alpha\int \tilde{\Psi}_m\tilde{\Psi}_m \,\mathrm{d}\tau = 2\int (\nabla_\alpha\tilde{\Psi}_m)\tilde{\Psi}_m \,\mathrm{d}\tau = 0.$$

Now $\delta\Lambda_m^k$ represents an arbitrary variation, so the vanishing of (1.5) requires

$$\hat{H}_{\text{nuc}}^m \Lambda_m^k \equiv \left[E_m(\mathbf{R}) + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \frac{1}{2}\sum_\alpha \left(-\frac{m}{M_\alpha}\right) \int \tilde{\Psi}_m \nabla_\alpha^2 \tilde{\Psi}_m \, d\tau + \frac{1}{2}\sum_\alpha \left(-\frac{m}{M_\alpha}\right) \nabla_\alpha^2\right] \Lambda_m^k = \varepsilon_m^k \Lambda_m^k, \quad (1.6)$$

in which the electronic energy, $E_m(\mathbf{R})$, appears as a potential energy term in the effective Hamiltonian for nuclear motion. The total molecular energy is therefore given by

$$\begin{aligned}\varepsilon_m^k &= \iint \Phi_m^k \hat{\mathscr{H}} \Phi_m^k \, d\tau \, d\mathbf{R} = \iint \tilde{\Psi}_m \Lambda_m^k \hat{\mathscr{H}} \tilde{\Psi}_m \Lambda_m^k \, d\tau \, d\mathbf{R} \\ &= \int \Lambda_m^k \hat{H}_{\text{nuc}}^m \Lambda_m^k \, d\mathbf{R}.\end{aligned}$$

where Λ_m^k satisfies (1.6).

The molecular wave functions (1.1) are not eigenfunctions of $\hat{\mathscr{H}}$: this is most readily seen by operating with $\hat{\mathscr{H}}$ on any one of the wave functions (1.1).

$$\begin{aligned}\hat{\mathscr{H}}(\tilde{\Psi}_m \Lambda_m^k) &= \left(\hat{H} + \frac{1}{2}\sum_\alpha \left(-\frac{m}{M_\alpha}\right) \nabla_\alpha^2 + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}\right) \tilde{\Psi}_m(\mathbf{r}, \mathbf{R}) \Lambda_m^k(\mathbf{R}) \\ &= \tilde{\Psi}_m \left(E_m(\mathbf{R}) + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \frac{1}{2}\sum_\alpha \left(-\frac{m}{M_\alpha}\right) \nabla_\alpha^2\right) \Lambda_m^k(\mathbf{R}) \\ &\quad + \sum_\alpha \left(-\frac{m}{M_\alpha}\right) (\nabla_\alpha \tilde{\Psi}_m).(\nabla_\alpha \Lambda_m^k) + \frac{1}{2}\sum_\alpha \left(-\frac{m}{M_\alpha}\right) (\nabla_\alpha^2 \tilde{\Psi}_m) \Lambda_m^k \\ &= \tilde{\Psi}_m \left(E_m(\mathbf{R}) + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \frac{1}{2}\sum_\alpha \left(-\frac{m}{M_\alpha}\right) \times \left[\nabla_\alpha^2 + \int \tilde{\Psi}_m \nabla_\alpha^2 \tilde{\Psi}_m \, d\tau\right]\right) \Lambda_m^k \\ &\quad + \sum_\alpha \left(-\frac{m}{M_\alpha}\right) \left[(\nabla_\alpha \tilde{\Psi}_m).(\nabla_\alpha \Lambda_m^k) + \frac{1}{2}(\nabla_\alpha^2 \tilde{\Psi}_m) \Lambda_m^k - \frac{1}{2} \Lambda_m^k \tilde{\Psi}_m \int \tilde{\Psi}_m \nabla_\alpha \tilde{\Psi}_m \, d\tau\right] \\ &= \varepsilon_m^k \tilde{\Psi}_m \Lambda_m^k + \sum_\alpha \left(-\frac{m}{M_\alpha}\right) \left[(\nabla_\alpha \tilde{\Psi}_m).(\nabla_\alpha \Lambda_m^k) + \frac{1}{2}(\nabla_\alpha^2 \tilde{\Psi}_m) \Lambda_m^k - \frac{1}{2} \Lambda_m^k \tilde{\Psi}_m \int \tilde{\Psi}_m \nabla_\alpha^2 \tilde{\Psi}_m \, d\tau\right]. \quad (1.7)\end{aligned}$$

The terms in square brackets cause the wave functions (1.1) to be coupled

together. For example, a typical coupling is represented by the matrix element

$$\iint \Phi_n^k \hat{\mathscr{H}} \Phi_m^l \, d\tau \, d\mathbf{R}$$

which, after using (1.7), becomes

$$\begin{aligned}\varepsilon_m^l \cdot \delta_{mn}\delta_{kl} &+ \int \Lambda_n^k \left[\int \tilde{\Psi}_n \sum_\alpha \left(-\frac{m}{M_\alpha} \right) (\nabla_\alpha \tilde{\Psi}_m) \, d\tau \right] . (\nabla_\alpha \Lambda_m^l) \, d\mathbf{R} \\ &+ \frac{1}{2} \int \Lambda_n^k \left[\int \tilde{\Psi}_n \sum_\alpha \left(-\frac{m}{M_\alpha} \right) (\nabla_\alpha^2 \tilde{\Psi}_m) \, d\tau \right] \Lambda_m^l \, d\mathbf{R} \\ &- \delta_{mn} \int \Lambda_n^k \left[\frac{1}{2} \int \tilde{\Psi}_m \sum_\alpha \left(-\frac{m}{M_\alpha} \right) (\nabla_\alpha^2 \tilde{\Psi}_m) \, d\tau \right] \Lambda_m^l \, d\mathbf{R}. \end{aligned} \tag{1.8}$$

Thus there are no matrix elements between different nuclear states associated with the same (non-degenerate) electronic state ($m = n$). But the wave functions are coupled together if $m \neq n$: this also includes the situation in which $\tilde{\Psi}_n$, $\tilde{\Psi}_m$ are degenerate. Now so long as the energies of $\tilde{\Psi}_n$ and $\tilde{\Psi}_m$ are well separated, the effect of the coupling terms will be small as the electronic wave functions vary slowly with changes in the nuclear coordinates. In this situation the coupling terms are usually ignored. The molecule then remains on one electronic potential energy surface, $E_m(\mathbf{R})$, for all motions of the nuclei. This is the basis of the "adiabatic" approximation as proposed by Born and Oppenheimer.[3] However, for degenerate, or near degenerate, electronic states the coupling terms may become very large and invalidate the Born–Oppenheimer approximation. The reason for this behaviour is most readily seen by examining a different form for the integral $\int \tilde{\Psi}_n \nabla_\alpha \tilde{\Psi}_m \, d\tau$, which appears in the matrix element (1.8).

First, the operator ∇_α is applied to each side of (1.3):

$$(\nabla_\alpha \hat{H}) \tilde{\Psi}_n + \hat{H}(\nabla_\alpha \tilde{\Psi}_n) = [\nabla_\alpha E_n(\mathbf{R})] \tilde{\Psi}_n + E_n(\mathbf{R})(\nabla_\alpha \tilde{\Psi}_n).$$

Multiplication of both sides by $\tilde{\Psi}_m$, followed by integration over space and spin coordinates, then gives

$$\int \tilde{\Psi}_m (\nabla_\alpha \hat{H}) \tilde{\Psi}_n \, d\tau + \int \tilde{\Psi}_m \hat{H} [\nabla_\alpha \tilde{\Psi}_n] \, d\tau = E_n \int \tilde{\Psi}_m \nabla_\alpha \tilde{\Psi}_n \, d\tau$$

which, from the Hermitian nature of $\hat{H}$, becomes

$$(E_n - E_m)^{-1} \int \tilde{\Psi}_m (\nabla_\alpha \hat{H}) \tilde{\Psi}_n \, d\tau = \int \tilde{\Psi}_m \nabla_\alpha \tilde{\Psi}_n \, d\tau. \tag{1.9}$$

Equation (1.9) shows clearly why the coupling terms cannot be ignored when the electronic states are not well separated in energy: for then, the electronic wave functions are very sensitive to changes in the nuclear coordinates.

The coupling between the various molecular wave functions, (1.1), has the effect of contaminating a given non-degenerate wave function, for example