Semi-empirical Self-consistent-field Molecular-orbital Theory of Molecules

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WILEY-INTERSCIENCE
a division of John Wiley & Sons Ltd
London–New York–Sydney–Toronto

Preface

In the summer of 1970, one of us (J. N. M.) had the opportunity of presenting a course of lectures on semi-empirical SCF–MO theory at the University of Nebraska, and at San Diego State College. In preparing these lectures we were particularly struck by the difference in philosophy between some of the principal workers in the field, and by the wide variation in the methods used to choose the parameters that enter these theories. Moreover the theories have changed rapidly over the last few years, and it must be confusing for the non-specialist to sort his way through the maze of initials ranging from CNDO/1 to MINDO/2. We hope in this book to play the role of pathfinders in this respect.

In writing the book we have in mind, primarily, the experimentalist who is interested in using theoretical methods to predict the results of possible experiments and to analyse his results. At the present time computer programs are readily available for many of the theories which we shall describe and the main problem that the experimentalist faces is which theory is the best for his particular data and how reliable is that theory. Although we have tried to answer these questions, we have not written a book for the complete novice in theoretical chemistry. We would not wish to encourage such a person to use the theories we describe without some knowledge of simple MO theories like Hückel theory. On the other hand we hope to show that SCF theories are not so complicated that they can only be understood and used by the professional theoretician.

Although Hückel theory has had many successes in theoretical organic chemistry we believe that it has now largely outlived its usefulness. The SCF theories which have replaced it are based on firmer theoretical foundations and they are more reliable for the prediction and understanding of quantitative data. We therefore begin the book by emphasizing some of the failures of Hückel theory.

In chapter 2 we describe the SCF theories of π electrons which were developed after 1953. The mathematical developments introduced in this chapter are sufficient to carry the reader through the more recent all-valence-electron theories which are described in chapter 3. These two chapters cover the properties of molecules both in their ground states and in excited electronic states. There has been some difficulty in getting parameters to fit both types of data, which is the reason that most books deal with one or the other. We shall however show that in the more recent theories parameters can be found which are adequate for both.

Chapters 4 and 5 give applications of the theories in the fields of chemical structure and reactivity and in magnetic resonance spectroscopy. These chapters contain some of the subsidiary theory needed to analyse the experimental data. For example, we discuss the theory of the ESR hyperfine constant before describing its interpretation in terms of electronic wave functions. We complete the book with a brief discussion of possible future developments and include two mathematical appendices.

The book lists over 350 references and these have been chosen from a fairly thorough literature search up to the middle of 1970. There is a much wider coverage for the all-valence-electron theories than for the early π-electron SCF theories as we feel that the latter are more widely available in earlier texts.

J. N. M.
A. J. H.

Symbols and abbreviations

Fundamental constants

e	electronic charge	4.803×10^{-10} e.s.u.
m	electronic mass	9.109×10^{-28} g
c	velocity of light	2.998×10^{10} cm sec^{-1}
$\hbar = h/2\pi$	Planck's constant	1.054×10^{-27} erg sec
k	Boltzmann's constant	1.381×10^{-16} erg degree^{-1}
a_0	Bohr radius	0.5292 Å

Operators

$\mathscr{H}$	The complete electronic Hamiltonian, or a general Hamiltonian
$\mathbf{H}$	a one-electron Hamiltonian not rigorously defined
$\mathbf{H}^c$	the core Hamiltonian (the terms in $\mathscr{H}$ which are functions of the coordinates of one electron)
$\mathbf{F}$	the self-consistent-field operator

$\mathbf{J}^2$, $\mathbf{J}_z$, $\mathbf{J}$, $\mathbf{J}^+$, $\mathbf{J}^-$, $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{I}^2$, etc. angular momentum operators

$\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$ del squared, which occurs in the kinetic energy operator

Wave functions

φ	an atomic orbital
ψ	a molecular orbital
Ψ	a complete wave function
α, β	spin wave functions

Integrals

$\int \cdots \mathrm{d}v$	integration over space coordinates
$\int \cdots \mathrm{d}\tau$	integration over space and spin coordinates
$\mathscr{H}_{rs} = \int \Psi_r \mathscr{H} \Psi_s \, \mathrm{d}\tau$	a matrix element of $\mathscr{H}$
$S_{rs} = \int \Psi_r \Psi_s \, \mathrm{d}\tau$	the overlap integral
$(\mu\nu \mid \rho\sigma) = \iint \varphi_\mu(1)\varphi_\nu(1)(e^2/r_{12})\varphi_\rho(2)\varphi_\sigma(2) \, \mathrm{d}v_1 \, \mathrm{d}v_2$	
$\gamma_{\mu\nu} = (\mu^2 \mid \nu^2)$	

Other symbols

A	electron affinity
c	an expansion coefficient
F^n, G^n	Slater-Condon parameters
$\mathbf{H}$	magnetic field
I	ionization potential
k	rate constant
K	equilibrium constant
$P_{\mu\nu}$	bond order
Z_M	nuclear charge
δ_{rs}	Kronecker delta ($= 0, r \neq s; = 1, r = s$)
ζ	Slater orbital exponent
π	polarizability factor
ρ	charge density

Energy conversion table

	erg molecule^{-1}	kcal mole^{-1}	eV	a.u.
erg/molecule	1	$1{\cdot}439 \times 10^{13}$	$6{\cdot}242 \times 10^{11}$	$2{\cdot}294 \times 10^{12}$
kcal/mole	$6{\cdot}947 \times 10^{-14}$	1	$4{\cdot}336 \times 10^{-2}$	$1{\cdot}594 \times 10^{-3}$
eV	$1{\cdot}602 \times 10^{-12}$	23·06	1	$3{\cdot}675 \times 10^{-2}$
a.u. (Hartree)	$4{\cdot}359 \times 10^{-11}$	627·5	27·21	1

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Chapter 1

The limitations of Hückel theory and the development of the self-consistent-field (SCF) method

Most chemists are familiar with the Hückel molecular orbital theory of π electrons, and many have followed the recent extensions of the theory to σ electrons. This theory has been very successful in explaining many properties of organic molecules, and has to a large extent superseded the more traditional resonance theory in the language of the experimental chemist. The stimulus of the work of Coulson, Dewar and Longuet-Higgins, and later of Hoffmann and Woodward, has shown that molecular orbital theory in its simplest form leads to quantitative predictions of molecular properties after only a trivial mathematical analysis.

The successes of this simple theory cover the field of molecular geometries, ground-state energies, reactivity and spectroscopic properties. There is no shortage of good books on the subject and we list a few of them in the bibliography.[1–3] Our objective in this chapter is to emphasize the points at which Hückel theory fails as a justification for the development of more comprehensive theories.

The history of calculations on small molecules like H_2 suggests that there is no simple way of obtaining exact solutions of the Schrödinger equation for many-electron atoms and molecules. By exact we mean that the calculated *total* energies have an accuracy comparable with those which can be generally obtained from experiment. Energy differences, deduced by spectroscopic methods, may of course cover a very wide range, depending on the type of spectroscopy used, and 'exact' solutions may show up badly when tested by the criteria of low-frequency spectroscopy.

'Exact' solutions of the electronic Hamiltonian—that is the Hamiltonian based on the Born–Oppenheimer approximation of stationary nuclei—have been obtained for simple molecules[4–6] like H_2, LiH and H_3 and one can expect exact solutions for molecules like H_2O within a few years. However, chemists are generally interested in far larger molecules than these, for which such exact solutions are not possible within the foreseeable future.

Between the extremes of Hückel theory and exact calculations there are many methods of calculating approximate wave functions. Most of these fall within the model called the self-consistent-field molecular-orbital (SCF–MO) method. In this one uses the concept of a molecular orbital, as being the wavefunction of one electron moving in the potential of the nuclei and the average effective potential of the other electrons. Within this model there are various levels of approximation. At the one extreme one has best wave functions of this type, calculated without any empirical parameters, which are called Hartree–Fock wave functions. At the other extreme one has semi-empirical π-electron theories such as that developed by Pople.[7]

To understand the various approximations that have been introduced into the SCF method we must first define the equations on which it is based. The derivation of these equations is not easy to follow without a good background in quantum mechanics, and we have therefore put this derivation in appendix 2 in order to carry the reader through to the more important parts of the book.

In Hückel theory the molecular orbitals ψ are written as a linear combination of atomic orbitals φ (the LCAO approximation)

$$\psi = \sum_{\nu} c_{\nu}\varphi_{\nu} \tag{1.1}$$

and are assumed to be solutions of the equation

$$\mathbf{H}\psi = E\psi \tag{1.2}$$

where $\mathbf{H}$ is a one-electron operator. If expression (1.1) is substituted into (1.2) we obtain

$$\sum_{\nu} c_{\nu}(\mathbf{H} - E)\varphi_{\nu} = 0. \tag{1.3}$$

The coefficients c_{ν} are most easily determined by multiplying (1.3) by one of the atomic orbitals φ_{μ} and integrating over all the three dimensional space.† This gives the so-called secular equations

$$\sum_{\nu} c_{\nu} \int \varphi_{\mu}(\mathbf{H} - E)\varphi_{\nu}\, \mathrm{d}v = 0 \tag{1.4}$$

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† More precisely one should multiply by the complex conjugate of φ_{μ}, but as most calculations of this type use real orbitals we shall ignore this feature throughout the book.

If we define the quantities $H_{\mu\nu}$ and $S_{\mu\nu}$ by

$$\int \varphi_\mu \mathbf{H} \varphi_\nu \, \mathrm{d}v = H_{\mu\nu}, \tag{1.5}$$

and

$$\int \varphi_\mu E \varphi_\nu \, \mathrm{d}v = E \int \varphi_\mu \varphi_\nu \, \mathrm{d}v = E S_{\mu\nu}, \tag{1.6}$$

then the equations have the form

$$\sum_\nu c_\nu (H_{\mu\nu} - E S_{\mu\nu}) = 0. \tag{1.7}$$

There is one equation of this type for each atomic orbital φ_μ in the set. To find their solutions the allowed energies are first determined by equating the secular determinant to zero

$$|H_{\mu\nu} - E S_{\mu\nu}| = 0, \tag{1.8}$$

and each energy is then substituted into (1.7) to determine the appropriate set of coefficients.

The essential feature of Hückel-type theories is that the operator $\mathbf{H}$ is not defined by the terms in the complete Hamiltonian of the molecule. Instead it is assumed that the integrals $H_{\mu\nu}$ are meaningful quantities whose values may be determined empirically, that is by fitting theory and experiment.

The theory finds its simplest form in the familiar π-electron theory, in which the energy of repulsion between electrons is ignored, or at best assumed to be a constant which is independent of the detailed distribution of electrons within the molecule. This type of theory is generally called an independent-electron theory, in the sense that the wave function and energy of a molecular orbital do not depend on the number of electrons occupying other molecular orbitals of the molecule. There are modifications of Hückel theory, the Wheland-Mann or the ω-method for example[1], in which some account is taken of electron repulsion, and these can be considered as the simplest form of SCF theories.

The empirical parameters of Hückel theory are usually given the symbols α and β, defined by

$$\alpha_\mu = \int \varphi_\mu \mathbf{H} \varphi_\mu \, \mathrm{d}v, \tag{1.9}$$

$$\beta_{\mu\nu} = \int \varphi_\mu \mathbf{H} \varphi_\nu \, \mathrm{d}v \tag{1.10}$$

which are called the coulomb and resonance integrals respectively. The overlap integrals $S_{\mu\nu}$ ($\mu \neq \nu$) may be taken as zero, as in Hückel π-electron theory, or they may be calculated from atomic orbital wave functions, as in Hoffmann's extended-Hückel theory of σ electrons[8].

At this point we shall list a few of the unsatisfactory features of Hückel theory which have provided the stimulation for the development of the more sophisticated theories which are to be described in this book.

1. In general, values of the Hückel parameters α and β are determined empirically by fitting theoretical calculations to observed data. However, the optimum value of the parameters depends on the nature of the experimental data that is under consideration. For example, the first ionization potentials of aromatic hydrocarbons correlate closely with the energy of the highest occupied Hückel π orbital if this is calculated with $\beta = -4{\cdot}0$ eV. For the same compounds, the energy of the first strongly allowed electronic transition (giving the so-called ^{1}La or *p*-band) is given by the difference in energy between the lowest vacant and highest occupied molecular orbitals calculated with $\beta = -2{\cdot}4$ eV. Finally, if we examine the correlation between the Hückel delocalization energy (that is the total energy less a value of 2β for each formal double bond) and the observed resonance energy (the difference between the total energy and that calculated on the basis of additive bond energies), then from the correlation line we deduce $\beta = -0{\cdot}7$ eV.†

From the very large difference between these three values for β one would conclude that the parameter represents a different combination of one-electron energies (nuclear attraction and kinetic energy) and two-electron repulsion energies, for each different type of data. This is what we find to be the case when we examine the relevant energy expressions of SCF theory.

2. Hückel theory is more successful for non-polar molecules, such as hydrocarbons, than for molecules with relatively polar bonds. It is more successful for alternant aromatic hydrocarbons (e.g. naphthalene), which in their ground states have a uniform distribution of π charge over the carbon atoms, than for non-alternant hydrocarbons (e.g. azulene), which have a non-uniform distribution of π charge. Thus the dipole moment of azulene, calculated from Hückel theory, is about seven times larger than the experimental value. This discrepancy arises from the neglect of electron repulsion which is inherent in the assumption that α is independent of the charge on the atom.

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† These parameters are all as deduced by Salem.[3]

3. In calculations on hetero-atomic molecules the number of empirical parameters (α_X, β_{XY}) needed to carry out a calculation may be very large whereas the amount of experimental data from which to determine these parameters may be relatively small. This problem is present to some extent in the semi-empirical SCF theories, but as these make use of a considerable amount of atomic spectral data it is not usually so severe. If in Hückel theory one attempts to take the coulomb integrals directly from atomic spectral data then one usually ends up with unreasonably large bond polarities, again because of the neglect of electron repulsion. Moreover, it is often necessary to allow for the fact that α_X for an X—Y molecular fragment depends on the nature of atom Y.

4. There are some molecular properties, notably the energies and intensities of some electronic absorption bands, which cannot be fitted at all by Hückel theory, or by any theory based on a one-electron Hamiltonian. For example, amongst the π molecular orbitals of benzene both the highest occupied and lowest unoccupied molecular orbitals are doubly degenerate. If the excitation energy is equated to the difference in the orbital energies, which would follow if electron repulsion were ignored, then one would predict a four-fold-degenerate excited state and one strong band in the absorption spectrum. It is known, however, that such an electronic excitation gives three excited states, which give two weak (symmetry-forbidden) bands in the absorption spectrum and one strong band.

There are several books[9–12] that describe in detail the theory of the electronic spectra of organic molecules, and we shall not cover this topic to any large extent in this book. We wish to emphasize however that the failure of Hückel theory to explain spectroscopic data played a large part in the initial development of the self-consistent-field theories we shall describe in this book.

The SCF molecular orbitals are defined by formally similar equations to (1.7) and (1.8). They are taken to be eigenfunctions of an operator **F**

$$\mathbf{F}\psi = E\psi \tag{1.11}$$

and if the LCAO expansion (1.1) is adopted, then the coefficients and energies are determined by the equations

$$\sum_{\nu} c_{\nu}(F_{\mu\nu} - ES_{\mu\nu}) = 0, \tag{1.12}$$

$$|F_{\mu\nu} - ES_{\mu\nu}| = 0, \tag{1.13}$$

where

$$F_{\mu\nu} = \int \varphi_{\mu}\mathbf{F}\varphi_{\nu}\, dv. \tag{1.14}$$

However, unlike the Hückel operator, **F** is well defined by the elements of the full Hamiltonian. Its matrix elements, $F_{\mu\nu}$, are given by expressions first derived by Lennard-Jones,[13] Hall[14] and Roothaan.[15]

$$F_{\mu\nu} = H_{\mu\nu}{}^{c} + \sum_{\rho}\sum_{\sigma} \mathrm{P}_{\rho\sigma}[(\mu\nu \mid \rho\sigma) - \tfrac{1}{2}(\mu\rho \mid \nu\sigma)] \tag{1.15}$$

H^{c} is called the core Hamiltonian for an electron. It consists of the kinetic energy operator for an electron and the potential energy between an electron and all atomic cores of the molecule.

$$\mathrm{H}^{c} = \frac{-\hbar^{2}}{2m}\nabla^{2} + \sum_{\mathrm{A}} V_{\mathrm{A}}, \tag{1.16}$$

where

$$\nabla^{2} = \partial^{2}/\partial x^{2} + \partial^{2}/\partial y^{2} + \partial^{2}/\partial z^{2}. \tag{1.17}$$

If all electrons are being specifically included in the calculation then V_{A} is the nuclear-electron potential energy equal to $-Z_{\mathrm{A}}e^{2}/r_{\mathrm{A}}$ (Z_{A} being the nuclear charge). In a π-electron model V_{A} would be the potential energy of the nuclei together with the repulsion of the σ electrons. The complete electronic Hamiltonian, $\mathscr{H}$, is made up of the core terms and the potential energy of repulsion of the electrons

$$\mathscr{H} = \sum_{i} \mathrm{H}^{c}(i) + \sum_{i<j} e^{2}/r_{ij} \tag{1.18}$$

It is usual in quantum-mechanical calculations on molecules to work in a system of units called atomic units in which the charge and mass of the electron and $\hbar$ are all taken as unity. In these units the unit of length is the Bohr radius $a_0 = 0{\cdot}5292$ Å and the unit of energy (called the Hartree) is 27·21 eV. In these units the complete Hamiltonian has the form

$$\mathscr{H} = -\sum_{i} \tfrac{1}{2}\nabla_{i}{}^{2} + \sum_{\mathrm{A}} V_{\mathrm{A}} + \sum_{i<j} r_{ij}{}^{-1} \tag{1.19}$$

The remaining terms in (1.15) give the effect of the electron interaction. We use the definition

$$(\mu\nu \mid \rho\sigma) = \iint \varphi_{\mu}(1)\varphi_{\nu}(1)(e^{2}/r_{12})\varphi_{\rho}(2)\varphi_{\sigma}(2)\, \mathrm{d}v_{1}\, \mathrm{d}v_{2} \tag{1.20}$$

which is to be interpreted physically as the repulsion between an electron distributed in space according to the function $\varphi_{\mu}\varphi_{\nu}$ (1) and a second electron having the distribution $\varphi_{\rho}\varphi_{\sigma}$ (2).

The final term to be defined in (1.15) is the bond order $P_{\rho\sigma}$ which is written

$$P_{\rho\sigma} = 2\sum_{k} c_{k\rho}c_{k\sigma}, \tag{1.21}$$

the summation extending over all *occupied* molecular orbitals ψ_k. In π-electron theory $P_{\rho\sigma}$ has special significance when ρ and σ are atoms joined together because it has been found to be linearly related to the length of the ρ—σ bond.

Expression (1.15) only applies to closed-shell electron configurations, that is when all occupied molecular orbitals contain two electrons. It therefore applies to the ground states of most molecules. For radicals, or most excited electronic states slightly different equations are required.[16]

Once the elements $F_{\mu\nu}$ and the overlap integrals $S_{\mu\nu}$ are known the SCF orbitals are obtained with the same ease as the Hückel orbitals. There are however two major difficulties. In the first place one can see from (1.15) that $F_{\mu\nu}$ depends on the bond orders, and these from their definition (1.21) can only be calculated when the orbitals, that is the solutions of (1.12) and (1.13), are known. The equations have therefore to be solved iteratively. A rough estimate is made of the coefficients $c_{k\rho}$ (usually these are taken as the coefficients obtained from a Hückel calculation), which then allows one to make an estimate of the bond orders and $F_{\mu\nu}$ integrals. The secular equations are then solved to give improved values of the coefficients. The cycle of the calculation can be repeated until the coefficients obtained by solving the secular equations are the same as those used to construct $F_{\mu\nu}$: that is the input and output coefficients are self-consistent. In practice if a reasonable first estimate is made, the SCF cycle is convergent, but divergent situations can be encountered.

The second difficulty in solving the SCF equations lies in the evaluation of the integrals involved in $F_{\mu\nu}$, particularly those two-electron integrals (1.20) in which the four orbitals are all on different atomic orbitals.

Except for one-electron atoms, atomic orbitals are not simple functions of the distance between the electron and the nucleus. Accurate atomic orbitals are either expressed in tabular form, $\varphi(\mathbf{r})$ tabulated as a function of r, the distance of the electron from the nucleus, or as a linear combination of simple algebraic functions. It is known from the asymptotic form of the solutions of the Schrödinger equation that at large r, $\varphi(\mathbf{r})$ varies as exp $(-kr)$, thus the most convenient functions from which to build up accurate atomic orbitals are the so-called Slater orbitals

$$\chi_{nlm}(k, \mathbf{r}) = Nr^{n-1} \exp(-kr) Y_{lm}(\theta, \phi) \qquad (1.22)$$

n is an integer, which corresponds to the principal quantum number. The $Y_{lm}(\theta, \phi)$ are the spherical harmonic functions which describe the angular variation of the orbital, and are labelled by the quantum numbers l and m.

If Slater orbitals are used in the LCAO expansion (1.1), that is the φ_ν are taken as χ or as some linear combination of such functions, then the three and four-centre integrals are difficult to evaluate even on a large computer. They must either be obtained by numerical integration or by a series expansion with relatively slow convergence. One of the reasons that approximate SCF schemes have been developed is to obviate the necessity for calculating such integrals. This development will be described in the coming chapters.

An alternative set of functions that have been used to build up atomic orbitals are gaussian functions which have a radial dependence $\exp(-kr^2)$. These do not have the correct asymptotic limit, but if enough of these functions are taken in a linear expansion then it is possible to get a reasonable representation of an atomic orbital. As a rough guide one can say that if a Slater orbital is replaced by a sum of 3 to 5 gaussians then the results of the SCF calculations obtained with the Slater or gaussian basis will be similar for most properties of chemical interest. Although one needs to use more gaussian orbitals than Slater orbitals to obtain the same accuracy in an SCF calculation, and therefore more two-electron integrals like (1.20) occur in the calculation, this is more than offset by the relative ease with which the integrals can be evaluated. The reason for this is that the product of two gaussian orbitals on different centres, $\varphi_\mu\varphi_\nu$ is equal to a third gaussian centred somewhere between the two[17]. Because of this all three and four-centre integrals reduce to two-centre integrals which are relatively easy to calculate.

There are several different ways in which gaussian orbitals have been used in SCF calculations. One approach has been to use gaussian orbitals just to calculate the two-electron integrals over Slater orbitals. Another approach has been to use them directly as the LCAO expansion functions in (1.1). In the latter method one may choose to use only spherical gaussians, and then angular functions like p and d orbitals are built up by taking combinations of off-nuclear gaussians. Alternatively one can use the so-called cartesian gaussians like $x\exp(-kr^2)$ which have an angular dependence like spherical-harmonic functions ($x = r\cos\theta$, has an angular variation like a p orbital). It is not the main task of this book to give a critical account of the large number of calculations made with gaussian orbitals, even on quite large organic molecules like benzene[18] and pyridine.[19]. At the present time better calculations can be made on medium-sized molecules using a gaussian basis than a Slater basis, however the balance between the two methods can change with an advance in computer design or the techniques of numerical analysis.

The number of molecular orbitals, obtained in an LCAO calculation is equal to the number of atomic orbitals in the expansion. If the molecule has $2n$ electrons then clearly the absolute minimum number of atomic orbitals needed is n. In practice the minimum number will be greater than n as it will consist at least of all the atomic orbitals that are occupied by electrons in the ground states of the separate atoms. For hydrocarbons this means one orbital for each hydrogen ($1s$) and five for each carbon atom ($1s$, $2s$, $2px$, $2py$, $2pz$). In the absence of symmetry in the molecule a non-empirical SCF calculation with n atomic orbitals in the expansion will require the calculation of n^4 two-electron integrals and the solution of the n secular equations. Either of these can be the limiting factor which determines the maximum size of a molecule that is amenable even to a minimum-basis non-empirical calculation.

However, if empirical methods are to be used, the size of the molecule that can be examined may be increased considerably. In the first place some of the n^4 two-electron integrals may be neglected or be given empirical values. In the second place it may be possible to consider in detail only the electrons in the outer shells of the atoms, using the argument that inner-shell electrons (e.g. the $1s$ electrons of carbon) are little affected by bond formation. Thus the number of atomic orbitals that may be considered in an empirical calculation may be significantly less than the number required for a non-empirical calculation.

There is one other justification for the empirical calculation, and this is that we know that even an exact Hartree–Fock calculation would not give accurate values of all the quantities we are interested in because it is not a solution of the Schrödinger equation. An example of this is the prediction[20] by the Hartree–Fock method that F_2 is unstable. However, an empirical calculation may be parameterized in such a way that for a family of compounds it does give reliable values of the experimental quantities of chemical interest. We will return to this point later in the book.

In the following chapters we deal firstly with the SCF developments of π-electron theory and then with the extension to σ electrons. Applications will be given to a wide range of chemical properties, both for ground and excited states, and to the interpretation of magnetic resonance properties. We will conclude by giving our view of the likely development of the subject.

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