

THE ELECTRONIC STRUCTURE OF ATOMS
AND DIATOMIC HYDRIDES

A Thesis submitted by

DONALD REES

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Mathematics Department,
Imperial College,
London, S.W.7.

Abstract

In Part I of this thesis the theory of the isoelectronic structure of atoms is discussed using the notion of an isoelectronic sequence in which the electronic energy is expressed as a perturbation expansion in terms of inverse powers of the nuclear charge. An empirical procedure is then developed in order to estimate the second and third order coefficients of this expansion, from which the nuclear magnetic shielding constants and ionization potentials are calculated.

Part II extends the theory of isoelectronic sequences of atoms to the calculation of the first order density matrix. It is shown that to first order the calculation of this matrix can be reduced to the solution of a number of one-electron equations which have been solved for the helium ground and ^3S states and also the lithium ground state. For these atoms mean values of one-electron operators have been calculated by integration of this density matrix. From the density matrix the natural orbitals also can be derived, and are found to be identical to first order with the unrestricted molecular orbitals.

The third part reviews the role of united atom theory as applied to light molecules. The Platt Electrostatic model of a diatomic hydride is modified by introducing a scale factor which depends on the internuclear distance. This enables the molecular virial theorem to be satisfied, improves the agreement with experiment of the internuclear distance and force constant, and still enables the theory to be interpreted electrostatically.

Part IV extends the theory of isoelectronic sequences to diatomic hydrides, using a scale factor which varies with both the charge of the second nucleus and internuclear distance. The energies to first order, the equilibrium internuclear distances and force constants are computed for some isoelectronic sequences and compared with experiment.

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CONTENTS

	<u>Page</u>
GENERAL INTRODUCTION	7
 PART I: ISOELECTRONIC SEQUENCES OF ATOMS	
Chapter 1: The perturbation expansion.	12
Chapter 2: Calculation of the expansion coefficients and applications to atomic systems.	32
 PART II: ANALYTICAL CALCULATIONS OF ATOMIC PROPERTIES	
Chapter 3: The double perturbation expansion and the F function technique.	60
Chapter 4: The direct calculation of the first order density matrix for atoms.	75
 PART III: THE ELECTRONIC STRUCTURE OF DIATOMIC HYDRIDES - A UNITED ATOM APPROACH	
Chapter 5: United atom theory and the Platt electrostatic model of diatomic hydrides.	101

	<u>Page</u>
Chapter 6: Scaling of the Platt electrostatic model of diatomic hydrides.	124
PART IV: ISOELECTRONIC SEQUENCES OF HYDRIDE MOLECULES	
Chapter 7: The perturbation expansion and equilibrium distance and force constant.	138
Chapter 8: Applications to the one, two and four electron sequences.	150
APPENDIX	163
REFERENCES	168

General Introduction

During the past thirty five years, the quantum mechanical study of atoms and molecules has been one mainly of application. Unlike elementary particle theory, the solution of every chemical problem may be given in principle by the quantum mechanics of Dirac, Heisenberg and Schrödinger. The Schrödinger equation for an atom or a molecule may be constructed and its solutions determine directly or indirectly using statistical mechanics all those properties which are studied in experimental chemistry. The theoretical study of atoms and molecules therefore involves no new fundamental laws and is reduced to the problem of finding the solutions of equations. Unfortunately, however, these equations are far too complex to be solved exactly and even if exact solutions could be obtained, because of the large number of variables involved, they would be far too unwieldy to use in any application. The main problem faced by quantum chemists has therefore been that of bridging the enormous gap between the solutions of the Schrödinger equation in principle and the practical

calculation of the properties of any specific molecules.

This formidable programme of applying quantum mechanics to atoms and molecules on which the mathematical physicists in the nineteen thirties embarked was, in many ways, limited and proceeded rather slowly. Consequently the criticism is often made today that pre-war research solved the easier problems in quantum chemistry, the harder problems therefore having to be faced in current research. That this is to a certain extent true in this field, as in any other, is obvious. The point to note, however, is that the formulations of all the different methods of applying quantum mechanics to atoms and molecules were laid in the nineteen thirties.

The whole research movement in quantum chemistry was, after the war, one of systematization and consolidation. The mathematical techniques of the thirties were carefully examined and rigorized and were applied to a much wider range of molecules (see, for example, Hall and Lennard-Jones, 1950; Hall, 1950 and 1951). The next significant movement in this field did not emerge until the mid nineteen fifties with the advent of electronic computers. Following on from the success of James and Coolidge, 1933, for the hydrogen molecule, interest was again directed to the

calculation of accurate wave functions rather than to the exploitation of less accurate ones. Calculations have now become feasible which earlier would have consumed a lifetime. All the programming of molecular calculations has involved considerable changes in the mathematical techniques used and will eventually induce many more.

The electronic computer, however, is not the quantum chemical panacea that had hitherto been supposed by scientists. During the last six years, it has become increasingly obvious that for computing methods to be used efficiently the analytical structure of the equations needs to be better understood. At about the same time it was also realized that analytical solutions are possible for a wider range of problems than had previously been appreciated (see for example Dalgarno and Stewart, 1956, Dalgarno and Lynn, 1957). There has thus emerged a renewal of analytical interests in the application of quantum mechanics to the electronic structure of atoms and molecules.

In accordance with this current movement in quantum chemistry, this thesis attempts to review and to extend

analytical methods using perturbation theory to study the electronic structure of atoms and diatomic hydrides. Even though Part I of this thesis discusses an empirical procedure and Part II utilizes a computer program, the framework of the method is essentially analytical.

Although analytical methods are extremely difficult to apply to large molecules, their significance in future research could well be of great importance. For example, in problems involving molecular reactions many subtle analytical techniques of the field theorists have already been taken over (Hall and Levine, 1964). Within the next few years it seems extremely likely that high powered mathematical analysis might indeed narrow the gap between the equations governing a chemical problem and the practical calculation of chemical properties.

PART I

ISOELECTRONIC SEQUENCES OF ATOMS

CHAPTER I

THE PERTURBATION EXPANSION

1.1 Introduction

One of the most fruitful ideas in the study of atomic structure has been that of an isoelectronic sequence. Its importance in the analysis of spectra has been considerable since the gross features of spectra depend very simply on the nuclear charge z , so that interpolations and extrapolations are easy and profitable. The importance of isoelectronic sequences in the theory of atoms was first appreciated by Hylleraas, 1930 who showed that the Schrödinger equation could be reformulated so that its solution could be expressed as a power series in inverse powers of z . The resulting dependence of z on the non-relativistic electronic energy of an atom therefore provided some justification for the semi-empirical formulas introduced earlier by spectroscopists (see, for example, Mozeley, 1913 and 1914).

Another novelty of this treatment is that the solution is obtained using perturbation theory instead of the more usual variation theory. In practice, however, it will be shown that the perturbation equations are usually solved by a variational method and can be computed to a high degree of accuracy (Hylleraas, 1930). A further advantage of this theory is that, by repeating the

calculation using a determinantal wave function, the variation of the correlation energy as a function of z can be determined (Linderberg and Shull, 1960). This and other applications will be discussed in part I of this thesis.

1.2 The perturbation expansion for non degenerate wave functions.

In order to discuss this perturbation technique, it is convenient to use reduced Hartree units. In these units, the non-relativistic Hamiltonian H governing the electronic motion of an atomic system is given by

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{z}{r_i} + \sum_{i,j} \frac{1}{r_{ij}} \quad (1.2.1)$$

where z is the nuclear charge and r_i and r_{ij} are the distances between the i^{th} electron and the nucleus and the j^{th} electron respectively. Equation (1.2.1) is obtained by transforming the total non-relativistic Hamiltonian (in ordinary units) for the electronic and nuclear motions into centre of mass co-ordinates and neglecting the nuclear motion and those electronic terms which depend on M^{-1} , where M is the nuclear mass; M being large compared with the electronic mass. The resulting Hamiltonian H is then transformed into reduced Hartree units.

An important step in this procedure is to introduce a new unit of charge $e' = \frac{1}{2}$ without changing the units of mass or of action. This is a form of scaling in which the unit of length is then z Bohrs and of energy z^2 Hartrees. Shull and Hall, 1959 have referred to these units as modified reduced Hartree units. In these new units the Hamiltonian now becomes

$$-\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{1}{r_i} + \frac{1}{z} \sum_{i,j} \frac{1}{r_{ij}} = H_0 + \frac{1}{z} H, \quad (1.2.2)$$

In this new form, the Hamiltonian is suitable for a perturbation expansion with expansion parameter z^{-1} , H_0 being regarded as the unperturbed Hamiltonian and H' as the perturbation. The corresponding wave function Ψ and energy W may now be expanded in powers of z^{-1} according to

$$\Psi = \psi_0 + \frac{1}{z} \psi_1 + \frac{1}{z^2} \psi_2 + \dots \quad (1.2.3)$$

$$W = W_0 + \frac{1}{z} W_1 + \frac{1}{z^2} W_2 + \dots \quad (1.2.4)$$

The Schrödinger equation

$$(H - W) \Psi = 0 \quad (1.2.5)$$

for the perturbed system may then be written

$$H_0 \sum_{n=0}^{\infty} \psi_n z^{-n} + H' \sum_{n=0}^{\infty} \psi_n z^{-n-1} = \sum_{n=0}^{\infty} z^{-n} \sum_{r=0}^n W_r \psi_{n-r} \quad (1.2.6)$$

Since Ψ and W are continuous functions of z^{-1} , it follows on equating the coefficients of like powers of

z^{-1} that

$$(H_0 - W_0) \psi_0 = 0 \quad (1.2.7)$$

and

$$(H_0 - W_0) \psi_s + H' \psi_{s-1} = W_s \psi_0 + \sum_{r=1}^{s-1} W_r \psi_{s-r}, \quad s \neq 0 \quad (1.2.8)$$

Equation (1.2.7) fixes ψ_0 as an eigenfunction of H_0 with eigenvalue W_0 , and in this section it will be assumed that for the particular atomic state under investigation, W_0 is nondegenerate. This ensures that $\bar{\psi} \rightarrow \psi_0$ and $W \rightarrow W_0$ as $z \rightarrow \infty$. Furthermore equation (1.2.7) can be solved exactly since it separates into one electron equations which are all of the hydrogen atom form. To satisfy the Pauli exclusion principle, ψ_0 will be a single determinant of the hydrogen atomic orbitals, since degeneracy is not at present being considered.

If equation (1.2.8) is multiplied throughout by ψ_0^* and the result integrated over all configuration space, the following recurrence relation is obtained

$$W_s = \int \psi_0^* H' \psi_{s-1} dT - \sum_{r=1}^{s-1} W_r \int \psi_0^* \psi_{s-r} dT \quad (1.2.9)$$

in particular

$$W_1 = \int \psi_0^* H' \psi_0 dT \quad (1.2.10)$$

The coefficients W_0 and W_1 can therefore be calculated directly from ψ_0 , W_1 being the mean value of the

perturbation averaged over the unperturbed wave function ψ_0 . Dalgarno and Stewart, 1956 prove the more general result that each term in the expansion of the wave function determines two terms in the expansion of the energy. So if ψ_1 can be found, it determines W_2 and W_3 . In practice, however, W_1 is difficult to find, and at present it is only possible to solve equation (1.2.8) for $s = 1$ for certain restricted forms of perturbation (see for example, Bates, 1961, page 178). The insertion of the particular perturbation operator $\sum_{i < j} \frac{1}{r_{ij}}$ into the differential equation governing ψ , has not yielded exact solutions in closed form for ψ . For many first order perturbation problems, however, it is necessary only to solve for the first order contribution to $|\psi|^2$ and not ψ . A discussion of this technique is given in part II of this thesis.

Alternatively the more usual method of discussing ψ_1 is to express it as an infinite expansion in terms of a complete set of functions, usually the eigenfunctions of H_0 . Thus if the eigenfunctions of H_0 are $\psi^0, \psi^1, \psi^2, \dots$ with eigenvalues $E_0, E_1, E_2 \dots$ respectively, where ψ^n and E_n , say, refer to the eigenfunction ψ_0 and eigenvalue W_0 respectively, the expansion of ψ_1 in terms of this set is

$$\psi_1 = \sum_{i=0}^{\infty} A_i \psi^i \quad (1.2.11)$$

where the A_i 's are to be determined. Again using the

completeness property of the ψ^i , the function $H' \psi_0$ ($=H' \psi^n$) may be written in the expanded form

$$H' \psi_0 = \sum_{i=0}^{\infty} H'_{in} \psi^i \quad (1.2.12)$$

where

$$H'_{in} = \int \psi^{in*} H' \psi^n dT \quad (1.2.13)$$

Substitution of the series (1.2.11) and (1.2.12) in equation (1.2.8) for $s = 1$, and using the property that the ψ^i are eigenfunctions of H_0 gives

$$\sum_i A_i (E_i - W_0) \psi^i + \sum_i H'_{in} \psi^i = W_1 \psi_0 \quad (1.2.14)$$

If the coefficients of ψ^i are now equated, the following results are obtained.

$$\begin{aligned} A_i &= H'_{in} / (E_n - E_i) \\ &= H'_{in} / (W_0 - E_i), \quad i \neq n \end{aligned} \quad (1.2.15)$$

for $i = n$, since $W_0 = E_n$

$$W_0 = H'_{nn} = \int \psi_0 H' \psi_0 dT \quad (1.2.16)$$

which is the result directly obtained in equation (1.2.10).

A_n is now determined by the requirement that $\bar{\Psi}$, correct to the first order, be normalized. $\bar{\Psi}$ may be written

$$\bar{\Psi} = \psi_0 + \frac{1}{Z} \sum_{n=0}^{\infty} A_n \psi^n + O\left(\frac{1}{Z^2}\right) \quad (1.2.17)$$

using the orthogonal properties of the ψ^i

$$\int \bar{\Psi}^* \bar{\Psi} dT = 1 + \frac{2}{Z} A_n + O\left(\frac{1}{Z^2}\right) \quad (1.2.18)$$

Now if correct to the first order

$$\int \bar{\Psi}^* \bar{\Psi} dT = 1 \quad (1.2.19)$$

then

$$A_n = 0 \quad (1.2.20)$$

Therefore, in terms of the eigenvalues of H_0 , ψ_1 may be written

$$\psi_1 = \sum_{\substack{i \\ i \neq n}} \frac{H'_{in}}{E_n - E_i} \psi^i, \quad (1.2.21)$$

Equation (1.2.20) may be substituted into equation (1.2.9) for $s = 2$, to obtain the second order energy W_2 . Using the orthogonal property of ψ_0 and ψ_1 , and integrating this series for ψ_1 over all configuration space, the second order energy W_2 is given by the well known summation formula

$$W_2 = \sum_{\substack{i \\ i \neq n}} \frac{H'_{in} H'_{ni}}{E_n - E_i} \quad (1.2.22)$$

Series expressions for the higher order energies and wave functions may be obtained in a similar way, (see, for example, Bates 1961).

To return now to the general series expansion for W , if the electronic energy is re-written in terms of the original reduced Hartree units, the expression becomes

$$W = W_0 z^2 + W_1 z + W_2 + W_3/z + W_4/z^2 + \dots \quad (1.2.23)$$

Equation (1.2.23) therefore represents the dependence of the

electronic energy W on z in terms of reduced Hartree units assuming that the zero order wave functions are nondegenerate.

1.3 The perturbation expansion for degenerate wave functions.

For a large number of atomic orbitals the perturbation method described in the preceding section needs to be modified before it can be applied. This is commonly due to the degeneracy of the zero order wave functions which arise because of the degeneracy of the hydrogen orbitals. Thus, in general, there will be a number of determinantal wave functions which are eigenfunctions of H_0 with the same energy eigenvalue. The appropriate zero order wave function will now be a linear combination of these determinants corresponding to the same energy. Therefore for such an atomic state, let it be assumed that there are t linearly independent determinantal eigenfunctions of H_0 which, with no loss of generality, are given by $\psi^0, \psi^1, \dots, \psi^{t-1}$ so that their respective eigenvalues $E_0, E_1, \dots, E_{t-1}$ are such that $E_0 = E_1 = \dots = E_{t-1}$. It may also be assumed that $\psi^0, \psi^1, \dots, \psi^{t-1}$ have been made orthonormal. As z becomes infinitely large,

the total wave function, must approach some solution ψ_0 of equation (1.2.7) whose eigenvalue is E_0 , that is, some linear combination

$$\psi_0 = \sum_{i=0}^{t-1} c_i \psi^i \quad (1.3.1)$$

where the c_i are to be determined, noting, however, the condition that if ψ_0 is normalized then

$$\sum_{i=0}^{t-1} |c_i|^2 = 1 \quad (1.3.2)$$

With this definition of ψ_0 equation (1.2.8) remains valid and consequently the expression (1.2.10) for the first order energy as being the mean of the perturbation averaged over ψ_0 . This result is not immediately useful however since the c_i 's are as yet unknown.

The correct linear combinations depend on the perturbation H' and may be obtained by substituting (1.3.1) for $s = 1$ together with the expansions (1.2.10) for

ψ , and

$$H' \psi^j = \sum_k H'_{kj} \psi^k \quad (1.3.3)$$

similar to expansion (1.2.11), where

$$H'_{kj} = \int \psi^{*k} H' \psi^j d\tau \quad (1.3.4)$$

This gives

$$(H_0 - W_0) \sum_i A_i \psi^i + \sum_{k=0}^{t-1} \sum_i c_k H'_{ik} \psi^i = W_1 \sum_{i=1}^{t-1} c_i \psi^i \quad (1.3.5)$$

If $i \geq t$, equating the coefficients of ψ^i on both sides of equation (1.3.5) gives

$$(E_0 - E_i)A_i = \sum_{k=0}^{t-1} c_k H'_{ik} \quad (1.3.6)$$

But, for $i < t$, $E_i = E_0$, so that

$$\sum_{k=0}^{t-1} c_k \{H'_{ik} - E_i \delta_{ik}\} = 0, \quad i = 0, 1, 2 \dots t-1 \quad (1.3.7)$$

Equations (1.3.7) form a system of homogeneous linear equations. Therefore, in order that equations (1.3.7) should admit of other solutions besides the trivial one

$$\det |H'_{ik} - E_i \delta_{ik}| = 0 \quad (1.3.8)$$

Equation (1.3.8) is referred to as the secular equation.

Since the H'_{ik} are known constants it is an equation of the t^{th} degree in E_i , and therefore has t roots

i.e. $E_{11}, E_{12}, \dots, E_{1t}$. Each value of E_{1i} , $i = 1-t$, gives on substitution into equation (1.3.7) the ratio of the c_i whose specification is completed by the unitary condition (1.3.2) provided all the roots E_{1i} are different thus completely determining the zeroth-order eigenfunction, $\psi_{0\ell}$, the subscript indicating the root of (1.3.8) to which the eigenfunction corresponds.

The expansion coefficients A_i of the first order wave function are given by equation (1.3.6), for $i \geq t$. In order that the total wave function Ψ be normalized to first order in z^{-1} each of the remaining coefficients A_i

for $i < t$, by a similar argument to that given in the preceding section must be put equal to zero. Thus ψ_i , may be written

$$\psi_i = \sum_{i \geq t} \frac{\sum_{k=t}^{i-1} c_k H'_{ik}}{W_0 - E_i} \psi^i \quad (1.3.9)$$

where $E_0 = W_0$ of (1.2.4). Having determined the correct zero order wave functions the development of the theory proceeds just as for the nondegenerate case, and the second order energy may be represented as an infinite series similar to that of (1.2.22). (see, for example, Bates 1961). The main point to note is that the perturbation completely removes the degeneracy in first order. Thus while in the limit of infinite z , the configuration $(1s)^2 (2s)^2$, ^1S has precisely the same energy as the configuration $(1s)^2 (2p)^2$ ^1S diagonalization of the matrix over the perturbation operator provides two different values for the respective first order energies. If, however, the symmetry of the two configurations is different, there is no degeneracy problem in the unperturbed wave function, since the off diagonal elements of the matrix are zero. For example, the state $(1s)^2 (2s)^2 S$ is degenerate with the configuration $(1s)^2 (2p)^2 P$, but the symmetry is different.

1.4 Introduction of a screening constant.

In section two it was pointed out that the isoelectronic sequences of atoms as given by equations (1.2.3) and (1.2.4) are derived by scaling the unit of charge in the form $e' = e\sqrt{z}$. To permit the scaling to be adjusted even more efficiently Dalgarno and Stewart, 1960, also Froman and Hall, 1961, introduced the concept of a screening factor, α , so that the modified charge is taken as $e' = e\sqrt{z-\alpha}$, the units of length and energy being respectively $(z-\alpha)$ Bohrs and $(z-\alpha)^2$ Hartrees, the units of mass and of action still remaining unchanged. Now the Hamiltonian H of (1.2.1) may be written in the form

$$H = \sum_i \left(-\frac{1}{2} \nabla_i^2 - \frac{(z-\alpha)}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}} - \alpha \sum_i \frac{1}{r_i} \quad (1.4.1)$$

and in terms of these modified units becomes

$$H = H_0 + \frac{1}{(z-\alpha)} H'(\alpha) \quad (1.4.2)$$

$$\text{with } H_0 = \sum_i \left(-\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right) \quad (1.4.3)$$

and

$$H'(\alpha) = \sum_{i < j} \frac{1}{r_{ij}} - \alpha \sum_i \frac{1}{r_i} \quad (1.4.4)$$

H_0 may be again treated as the unperturbed operator and H' as the perturbation, both of which now depend on the constant α . It is clear that from the form of (1.4.4) for suitable positive values of α the magnitude of the perturbation H' may be much reduced. In precisely the

same manner as in the previous discussion the wave function is now expanded as

$$\Psi = \psi_0' + \frac{1}{z-\alpha} \psi_1' + \frac{1}{(z-\alpha)^2} \psi_2' + \dots \quad (1.4.5)$$

and the energy as

$$W = W_0' + \frac{1}{z-\alpha} W_1' + \frac{1}{(z-\alpha)^2} W_2' + \dots \quad (1.4.6)$$

Because the unperturbed Hamiltonian H_0 is exactly the same as before, ψ_0' will be a sum of determinants or else a single determinant of the hydrogen atomic orbitals depending on whether W_0' is degenerate or not. The perturbation equations of sections two and three still apply remembering the perturbation is now $(z-\alpha)^{-1}$ and not z^{-1} with the perturbation H' given by (1.4.4). The ψ_i' and W_i' , $i \geq 1$, are now functions of α , however. In the original reduced Hartree units the electronic energy whether degenerate or not has the form

$$W = (z-\alpha)^2 W_0' + (z-\alpha) W_1' + W_2' + W_3' (z-\alpha)^{-1} + \dots \quad (1.4.7)$$

with a similar expression for the wave function Ψ .

The first coefficient W_0' is the appropriate eigenvalue of H_0 corresponding to the relevant atomic state. For the non-degenerate case, W_1' is the mean value of the perturbation and depends on α . When there is degeneracy, W_1' is obtained by diagonalizing the matrix whose elements are the matrix elements of H' .

The first three terms in expression (1.4.7) may be expanded in terms of a quadratic polynomial in z , and therefore they are no more general than the usual z^{-1} expansion. The fourth term, however, is of quite a different form and will lead to different results if the series is broken off at this or any later point.

1.5 The choice of α with applications to the problem of convergence

The introduction of the screening constant α into the perturbation allows for the screening of the nucleus by the electrons and as such is a form of scale factor. As yet, however, α still remains unspecified and one therefore needs some further criterion so that α may be completely determined (Froman and Hall, 1961). The usual method adopted for the choice of α , is the value of α which minimizes the electronic energy; this is referred to as the minimum energy principle. In practice α is chosen so that the first two terms in the energy are minimized. This is the lowest energy obtainable using only ψ'_0 . The scale factor α is then determined by minimization so that

$$\frac{dW}{d\alpha} = -2(z-\alpha)W_0' - W_0' + (z-\alpha) \frac{dW_0'}{d\alpha} = 0 \quad (1.5.1)$$

Now W_0' is given by

$$\int \psi_0'^* H_0 \psi_0' dT = \int \psi_0'^* \left(\sum_{i < j} \frac{1}{r_{ij}} - \alpha \sum_i \frac{1}{r_i} \right) \psi_0' dT \quad (1.5.2)$$

Therefore differentiating W_0' with respect to α

$$\frac{dW_0'}{d\alpha} = - \int \psi_0'^* \left(\sum_i \frac{1}{r_i} \right) \psi_0' dT \quad (1.5.3)$$

Since ψ_0' is an eigenfunction of H_0 the virial theorem is satisfied (see appendix) so that

$$W_0' = - \frac{1}{2} \int \psi_0'^* \left(\sum_i \frac{1}{r_i} \right) \psi_0' dT \quad (1.5.4)$$

Substituting equations (1.5.2) and (1.5.3) into (1.5.1) gives

$$\frac{dW}{d\alpha} = - W_0' = 0 \quad (1.5.5)$$

and to this approximation the energy is $(z-\alpha)^2 W_0'$ where α is determined from equation (1.5.5).

Another choice of α might be that which makes σ^2 the mean square deviation of the energy, least, where

$$\sigma^2 = \int |H\psi - \langle H \rangle \psi|^2 dT \quad (1.5.6)$$

and where ψ is any normalized trial wave function, $\langle H \rangle$ denoting the mean value of the Hamiltonian with respect to ψ . Therefore using only ψ_0' , α may be determined from

$$\frac{d}{d\alpha} \int |H \psi'_0 - \langle H \rangle \psi'_0|^2 dT = 0 \quad (1.5.7)$$

Equation (1.5.7) has the theoretical advantage that the value of σ^2 found in this way gives a lower bound to the energy using the Weinstein relation (Weinstein, 1934) viz.

$$W \geq (z-\alpha)^2 W_0^1 + (z-\alpha)W_1^1 - \sigma \quad (1.5.8)$$

Recalling also that the variation principle (see Bates, 1961) gives the first two terms of (1.4.7) as an upper bound to the energy, it follows that when σ^2 is least the difference between this upper bound and the lower bound given by Weinstein is least.

A further criterion for α is that which determines the best possible convergence of the series. Now no mention has hitherto been made of the convergence of the series with either z^{-1} or $(z-\alpha)^{-1}$ as expansion parameter. This, in one sense, is a subsidiary issue since one merit of the isoelectronic series for atoms lies in the fact that they have asymptotic properties so that a finite number of terms may be a good approximation to the energy. The convergence problem is, nevertheless, difficult for the general isoelectronic expansion and has not been fully investigated except in a few cases

(see, Titchmarsh, 1958) Kato, 1951, has considered the problem for the Helium-like series and has shown that it converges strictly at least for $z \geq 8$. From a theoretical point of view this result is highly significant since, using isoelectronic sequences, the mathematical existence of the ground state of the Helium like ions was finally established. Froman and Hall, 1961, remark that for atoms with larger number of electrons the convergence is probably poorer. This last criterion for α is therefore difficult to apply in the general case. Froman and Hall, 1961, however, have considered this problem for the Helium-like atom by using a modification of the Kato argument. They have shown that the value of α so that the two electron series should converge for the lowest possible value of z is 0.35 and that this limit for z due to scaling gives $z = 2.64$. Table (1.5), (Froman and Hall, 1961,) shows the values of $z_{\min}$ for various values of α such that the He-like series converges at least for $z \geq z_{\min}$. It will be observed that the improvement in convergence is appreciable. It will also be noticed that although the choice of α which minimizes the first two terms of the energy does not ensure the most rapid convergence, the improvement in the

Table 1.5

	α	$z_{\min}$
Hylleraas expansion	0	7.64
Least O^-	$\frac{1}{8}$	5.86
$W_1 = 0$	$\frac{5}{16}$	3.18
Best α	0.35	2.64

Table 1.5

convergence compared with that of the original Hylleraas expansion is still appreciable and in any case does not differ greatly from that obtained when α is put equal to 0.35. This point will again be stressed in part IV of this thesis when the theory of isoelectronic sequences is developed for hydride molecules. It is of interest to note that the best value of α , 0.35, also appears in the Slater rules for screening constants.

It is clear therefore from the above discussion that an expansion in terms of $(z-\alpha)^{-1}$ yields a more accurate estimation of the electronic energy from the first few terms than from the same number of terms of the earlier one using z^{-1} . The introduction of a screening constant is also in greater accord with physical anticipations than the z^{-1} expansion.

Froman and Hall, 1961 comment that since free negative ions of more than one or perhaps two charges are not stable and will eject an electron, the nuclear charge of a many-electron atom cannot therefore be reduced much below that of the electrons without drastically changing the situation and hence the wave function. The wave function might then be expected to become considerably more diffuse. This can only be achieved by the wave function when expanded in terms of z^{-1} if the series diverges and for this to occur for some positive z the higher powers of z^{-1} must remain large. For the $(z-\alpha)^{-1}$ expansion, however, the series can also diverge as z approaches α . It might therefore be argued that the screening constant should have the significance that it gives approximately the nuclear charge for which the system is unstable.

CHAPTER 2

CALCULATION OF THE EXPANSION
COEFFICIENTS AND APPLICATIONS
TO ATOMIC SYSTEMS

2.1 Introduction

The theory of isoelectronic sequences of atoms as described in Chapter 1 of this thesis is completely general and applies to any system of atoms. The main difficulty, however, lies in the application of these sequences to specific atomic systems, and, as a result, this problem has recently received some attention in the literature. The source of this difficulty is the inability to solve the perturbation equations exactly for the higher order contributions to the wave function, making it impossible therefore, to provide exact values of the coefficients in the expansion of the electronic energy. For the many electron atom the only two coefficients that can be determined exactly are the first two of (1.2.4), (see section 2.2), the whole theory being so constructed that the zero order wave function is accurately known. It becomes necessary, therefore, to rely on approximate methods. Chief amongst these is the variation method used, for example, by Hylleraas, 1930 as mentioned in the previous chapter. This method has been extremely successful in estimating a number of the coefficients of two and three electron systems but has the disadvantage that for larger systems there are

computational difficulties involved in estimating the higher order coefficients of the energy expansion. As a result, the usefulness of isoelectronic sequences as a compact and direct method of predicting experimental results for atoms seems to justify the introduction of semi-empirical methods for determining the expansion coefficients. Such methods have the advantage of being able to include in their data the best current theoretical and experimental results from which the coefficients may be determined.

In this chapter, the various applications of isoelectronic sequences to atomic problems is described together with a discussion of an empirical procedure for calculating coefficients of isoelectronic series for the ground state energies of a number of atomic systems using experimental data. It is further shown that such a technique requires a careful investigation of relativistic terms even for systems with small nuclear charge.

2.2 Exact calculation of the first two coefficients in the energy expansion.

The first task in applying isoelectronic sequences to atomic problems is to determine the coefficients in the energy expansion. Now as already mentioned W_0 and W_1 ,

may be determined exactly, since for an N electron atom, ψ_0 may be written in terms of the hydrogen atomic orbitals $\phi_1, \phi_2, \dots, \phi_N$ where the $\{\phi_i\}$ include components of spin and are also orthogonal. If, corresponding to a particular state and configuration, an eigenfunction u_0 of H_0 as defined by (1.2.2) is given by

$$u_0 = (N!)^{-\frac{1}{2}} \text{Det}\{\phi_1(1) \phi_2(2) \dots \phi_N(N)\} \quad (2.2.1)$$

then from equation (1.2.7)

$$W_0 = \int u_0^* H_0 u_0 d\tau \quad (2.2.2)$$

[If the state is non-degenerate, then $u_0 = \psi_0$. On the other hand if degeneracy occurs, u_0 is a member of the set $\{\psi_0^i\}$ of (1.3.1). In both cases, however, W_0 is given by (2.2.2)]. On substituting (2.2.1) into equation (2.2.2), the first order energy W_0 is given by

$$W_0 = \sum_{i=1}^N \int \phi_i^*(1) \left[-\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right] \phi_i(1) d\tau \quad (2.2.3)$$

(For details see, for example, Eyring, Walter, and Kimball, 1960). The first coefficient W_0 is thus the sum of contributions of $-\frac{1}{2}$ for each (1s) electron and of $-\frac{1}{8}$ for each (2s) or (2p) electron. Hence, for the general atomic configuration $(1s)^2 (2s)^p (2p)^q$,

$$W_0 = -1 - \frac{1}{8}(p+q) \quad (2.2.4)$$

and is therefore independent of the symmetry of the state. The coefficient W_1 is slightly more complicated to obtain than W_0 . If, for the non-degenerate case, ψ_0 is given by (2.2.1) then substitution of this determinantal form for ψ_0 into (1.2.10) yields

$$W_1 = \frac{1}{2} \sum_{ij} \{ [ij/ij] - [ij/ji] \} \quad (2.2.5)$$

where

$$[ij/k\ell] = \int \phi_i^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_k(1) \phi_\ell(2) d\tau_1 d\tau_2 \quad (2.2.6)$$

The integral $[ij/ij]$ of (2.2.5) is known as the 'coulombic integral' and $[ij/ji]$ as the 'exchange integral'. These integrals may be evaluated exactly by expanding $\frac{1}{r_{12}}$, the electrostatic repulsion in terms of spherical harmonics (for details see Eyring, Walter and Kimball, 1960). For the degenerate case the matrix elements of the perturbation involve similar integrals which may be evaluated directly before diagonalization. Integrals of the type (2.2.6) between various atomic orbitals are listed in Coudon and Shortley, 1951. Furthermore Linderberg and Shull, 1960, have evaluated W_0 and W_1 for both degenerate and non-degenerate states of all atoms with less than eleven electrons. A sample of these coefficients for the

ground states of a number of atoms are taken from Linderberg and Shull and appear in table 2.7. For the energy expansions in terms of $(z-\alpha)^{-1}$, it is easily seen either by evaluating the coefficients W'_0 and W'_1 directly and invoking the atomic virial theorem or else by expanding $(z-\alpha)^2$ and equating coefficients of z^2 and z that

$$W'_0 = W_0 \quad (2.2.7)$$

and

$$W'_1 = W_1 + 2W_0\alpha \quad (2.2.8)$$

2.3 Theoretical determination of the higher order energy coefficients.

The difficulties encountered in calculating the higher order coefficients of the energy expansion as discussed in the introductory section demand that the isoelectronic expansion for each atomic state be discussed separately. The sequence which has received the most attention in this respect is that of the ground-state of helium. Of the many electron atoms it is by far the simplest, the repulsive energy of the electrons reducing to one term. Hylleraas, 1930, succeeded in calculating the coefficients W_2 and W_3 by a variational method, and estimating W_4 , W_5 , W_6 with the aid of a scale factor. A similar technique was again used by

Hylleraas and Midtdal 1956 and 1958, to improve Hylleraas' estimates. In their calculation, W_2 was again determined variationally together with the non-relativistic energies of the ions for $1 \leq z \leq 16$ and W_3, W_4, W_5 and W_6 fitted to give the exact non-relativistic energies for H^∞ , He and Li^+ with a compromise between the computed values for Be^{++} and O^{6+} . This was the most accurate result until recently when Knight and Scherr, 1962 succeeded in estimating the first eleven coefficients of the helium sequence each to a high degree of accuracy. This calculation was performed by using the variation-perturbation technique due to Hylleraas by means of which variationally determined wave functions up to the fifth order were used to estimate the coefficients. The series truncated after these eleven terms suffice to furnish an extremely accurate eigenvalue for the helium ground state giving the energy as -2.90372425 reduced Hartrees (H_R) which differs only in the seventh decimal place from the 1078-term value of $-2.903724375 H_R$ as obtained by Pekar, 1958 and 1959. Table 2.1 shows a comparison between the recent calculations of Knight and Scherr and the coefficients as computed by Hylleraas and Midtdal. It will be observed that this recent value of W_2 clearly shows that the Hylleraas-Midtdal value has

still not converged to the extent they report (Hylleraas and Midtdal, 1958)

Table 2.1 Higher Order Coefficients for Helium

Ground State in H_R Units.

n	W_n [a]	W_n [b]
2	-0.157666254	-0.157657 ₅
3	0.008698679	0.008535
4	-0.000888302	-0.00034
5	-0.00103710	-0.00082
6	-0.00061284	-0.00244 ₅
7	-0.00037161	
8	-0.0002425	
9	-0.0001660	
10	-0.0001158	
11	-0.0000836	

[a] Knight and Scherr, 1962, [b] Hylleraas and Midtdal, 1958.

The results in table 2.1 may be easily adjusted to permit the introduction of the screening constant α . For full details, see Froman and Hall, 1961.

For atoms of more than two electrons, variational

calculations of the higher order coefficients in the energy expansion are much more difficult. Linderberg, 1962 has computed an estimate for the coefficient W_2 by variational means for a number of two, four, and six electron states. This coefficient is important since it plays the role of a reference point on the energy scale for systems where $z \rightarrow \infty$. Linderberg's estimate of W_2 is in actual fact an upper bound obtained by minimizing a functional which is dependent on an approximate form for the first order wave function. A sample of his results is given in table 2.7 in comparison with those obtained by empirical means using the method described in the next section of this thesis.

2.4 Empirical determination of the higher order energy coefficients

Before any empirical scheme can be developed to determine the higher order energy coefficients of the series (1.2.4), it is immediately clear that the experimental or total energy contains a number of relativistic effects in addition to its non-relativistic contribution W . It is therefore important to determine to what extent these relativistic terms effect the total

energy. Froman, 1958, has shown that for atomic systems with low nuclear charges the relativistic effects are relatively negligible. These effects, however, become rapidly important and indeed dominant for systems of higher z .

Now the present calculation is confined to the determination of the coefficients of the energy series of light atoms with comparatively low nuclear charge, and it is therefore reasonable to suppose on the basis of Froman's paper that the relativistic contributions to the experimental energies are not appreciable.

Accordingly for low values of z the experimental ionization potential I_E^n of an isoelectronic ion does not differ appreciably from the non-relativistic ionization potential $I_{NR}^n(z)$, which, from the previous discussion, may be expressed in terms of the series

$$I_{NR}^n(z) = a_2^n z^2 + a_1^n z + a_0^n + \frac{a_{-1}^n}{z} + \frac{a_{-2}^n}{z^2} + \dots \quad (2.4.1)$$

where n corresponds to the number of electrons. In actual fact, for reasonable accuracy, the spin orbit contribution to the energy, which is, for low z , the major relativistic contribution, was eliminated from I_E^n , the result being regarded as a reasonable estimate of I_{NR}^n . A discussion of the elimination of the spin-orbit energy

contribution together with the other relativistic corrections is given in the following section. Since the values of a_2 and a_1 are known (Linderberg and Shull, 1960), the first step in the evaluation of these higher-order coefficients was to subtract these known terms from $L_{NR}^n(z)$ to yield the remainder $X^n(z)$ where

$$X^n(z) = a_0^n + \frac{a_{-1}^n}{z} + \frac{a_{-2}^n}{z^2} + \dots \quad (2.4.2)$$

Using expression (2.4.2) an attempt was made to fit the constants a_0 , a_{-1} for various atoms by the method of least squares, using six experimental values of the ionization potentials (Moore, 1949) for each configuration to determine $X^n(z)$. An attempt to fit a_{-2} by this method led to ill-conditioning of the normal equations and had to be abandoned. Also, the constants a_0 and a_{-1} obtained in this way gave an extremely poor fit. Furthermore, since for a particular atomic configuration the calculated values of $X^n(z)$ did not necessarily decrease with increase of z , it was concluded that the constants a_0 and a_{-1} were still extremely sensitive to the remaining relativistic corrections.

The experimental ionization potentials were again modified by subtracting off the other relativistic effects, a discussion of which occurs in the following section, and values of a_0 and a_{-1} recalculated.

2.5 Relativistic corrections.

Relativistic calculations for many electron systems are at present difficult and complicated. One of the main reasons for this is the lack of a complete relativistic theory for many electron systems. As a result the one particle theory of Dirac which is relativistically covariant is usually used to discuss the relativistic effects of each electron and these effects are assumed additive for a many electron atom. The disadvantage of this procedure is that such relativistic estimations can never account for many particle interactions such as spin-other orbit interactions for example, and must therefore be included separately. Another refinement to relativistic calculations is to include radiative corrections, in particular the lowest-order one - electron correction (Lamb Shift). (For an account of these see, for example, Bethe and Saltpeter, 1957).

For the purposes of the present problem of modifying the ionization potentials by subtracting off the relativistic corrections, one electron effects only were considered and with no account taken of radiative corrections. It is sufficient therefore to consider the

Pauli approximation to the Dirac relativistic equation for an electron with no external magnetic field. The relativistic Hamiltonian H_{Rel} in reduced Hartrees is given by

$$H_{\text{Rel}} = -\frac{1}{2} \nabla^2 - \frac{Z}{r} - \frac{\alpha^2}{8} \nabla^4 + \alpha^2 \frac{Z}{4r^3} \underline{L} \cdot \underline{\sigma} - \frac{\alpha^2}{4} Z \frac{1}{r^2} \frac{\partial}{\partial r} \quad (2.6.1)$$

where the electron is assumed to have a Coulomb potential, α being the fine structure constant, $\underline{L}$ the orbital angular momentum and $\underline{\sigma}$ the Pauli spin matrix (see, Condon and Shortley, 1951). The first two terms of H_{Rel} constitute the simple non-relativistic Hamiltonian; the third is the first approximation to the effect of variable mass and the fourth is the spin-orbit term; the last term is peculiar to the Dirac theory and is known as the contact term.

It may be shown (Condon and Shortly, 1951) that the first order contribution to the relativistic energy given by the third term of (2.6.1) using scaled hydrogen orbitals is

$$E_1 = -\frac{\alpha^2 \pi^4}{2n^4} \left(\frac{n}{\ell + \frac{1}{2}} - \frac{3}{4} \right) \quad (2.6.2)$$

where π is the scale factor, and n and ℓ are the total and azimuthal quantum numbers of the hydrogen orbital.

Furthermore the contribution to the energy of the contact term using the first order perturbation over scaled hydrogen functions is

$$E_2 = \frac{\alpha^2 \eta^3 z}{2n^3} \quad \text{for S states} \quad (2.6.3)$$

$$= 0 \quad \text{for states other than S}$$

The energy contribution of the spin orbit term of (2.6.1) is somewhat difficult to estimate since it becomes indeterminate for S states as a result of the divergence of the integral $\int \frac{1}{r} U^1(r) \psi^2 d\tau$ and the vanishing of $\underline{L} \cdot \underline{\sigma}$. This is simply a consequence of the approximation procedure involved in deriving equation (2.6.1), and careful examination of this approximation shows that the spin-orbit term vanishes (see, for example, Bethe and Saltpeter, 1957). For states other than S states, first order perturbation theory gives determinate results and the spin orbit correction may be estimated from (1.2.1). An alternative method of accounting for the spin-orbit effect is to eliminate it by averaging over the experimental multiplet energies with weights equal to their degeneracy. This latter approach was, in fact, adopted in this calculation, thus leaving only $(E_1 + E_2)$ for each electron to be subtracted off from each of the averaged experimental energies.

The scaled form of equations (2.6.2) and (2.6.3) now enables the introduction of the scale factor $\eta = (z - \gamma)$, as described in Chapter I, where γ is the screening constant. This produces the desired physical effect of screening the nucleus from an electron by the electronic cloud formed by the inner electrons, and therefore might describe the relativistic contribution of a single electron more accurately. For each ion, γ was determined by minimizing its non-relativistic energy with respect to γ . It was found, however, that, in this approximation, the best relativistic estimates were obtained when the relativistic contributions of the 1s electrons in the two ions, whose energies are subtracted to find the ionization potentials, were considered equal. This is equivalent to taking the γ 's for the two ions under consideration to be equal when estimating the relativistic effects of the 1s electrons. Since in this problem systems of not more than six electrons were considered, this assumption is the same as that made by Scherr, Silverman, and Matsen, 1962 when estimating relativistic corrections for atoms, namely that the relativistic contribution of a closed shell is a constant independent of the number of electrons in outer shells.

2.7 Results and discussion.

Table 2.7 lists the coefficients in the energy expansion for atomic systems for $2 \leq N \leq 6$, where W_2^n and W_3^n are the results of the fitting technique described. The ionization potentials calculated from the coefficients in table 2.7 agree with the modified experimental energies to within 0.003 H. Also the electron affinity of Li- was calculated to be 0.014 H as compared with the extrapolated value 0.018 H by Holþien, 1960.

In table I are also included Linderbergs theoretical estimates of W_2^4 and W_2^6 as discussed in section 2.3, together with other estimates of the coefficients by Scherr, Silverman, and Matsen, using a similar fitting technique to that already discussed. It may be seen that there is reasonable agreement for the estimates of W_2^n but that the estimates for W_3^n differ appreciably. One of the chief reasons for this is that Scherr, Silverman, and Matsen, 1962 include the Lamb Shift as an extra contribution to the relativistic corrections before subtracting off the net relativistic effects (expressed as a descending power series) from the ionization potentials and applying the least squares procedure to the series for $X^n(z)$. This same calculation has been performed by

Table 2.7

Total Energy $W^n(z)$ of Isoelectronic Ions in the Form

$$W^n(z) = W_0^n z^2 + W_1^n z + W_2^n + W_3^n z^{-1} + \dots$$

n	W_0^n	W_1^n (a)	W_2^n	W_3^n
2	-1	0.625	-0.15766	+0.00854 +0.008690 (c)
3	-1.125	1.022805	-0.4014 ₆ -0.4089 (b) -0.4050 (c)	-0.058 ₈ -0.014 (b) -0.0302 (c)
4	-1.25	1.559274	-0.858 ₇ -0.880 (b) -0.84 (c) -0.8450 (d)	-0.181 ₆ -0.04 (b) -0.32 (c)
5	-1.375	2.327526	-1.79 ₇ -1.843 (b)	-0.59 ₂ -0.18 (b)
6	-1.5	3.258865	-3.20 ₁ -3.253 (b) -3.2245 (d)	+1.1 ₆ +0.49 (b)

W_0^n , W_1^n calculated theoretically; W_2^n , W_3^n fitted.

(a) Linderberg and Shull, 1960.

(b) Scherr, Silverman, and Matsen, 1962.

(c) Scherr and Silverman, 1962.

(d) Linderberg, 1962.

Scherr and Silverman, 1962 using improved estimates of the leading expansion coefficients in the power series for the relativistic effects (including the Lamb Shift) which may be obtained from the highly accurate and theoretical relativistic calculations of Pekeris, 1958, and Weiss, 1961. Another reason for this disagreement in the estimate of W_3^n is that both calculations by Scherr et al include screening constants in the expansions of the ionization potentials as well as in the series representing the relativistic effects. The coefficients of the energy expansion in powers of z^{-1} may then be recovered from those in the expansion in powers of $(z-\alpha)^{-1}$ (Scherr et al, 1962).

That the relativistic effects play such a dominant role in the determination of the higher order coefficients of the non-relativistic energy expansions for atoms of low nuclear charge z is, in retrospect, obvious. Since although, for such systems, the non-relativistic energy is exceedingly large in magnitude compared with its relativistic correction terms, the removal of the zero- and first-order contributions to the non-relativistic energy, in the fitting procedure, increases the relative magnitude of the relativistic contribution in the remainder sufficiently to interfere with the

determination of the higher order coefficients. This probably explains why, with no provision for the removal of the relativistic energy, an attempt to estimate W_k^n by the method of least squares produced ill-conditioned normal equations. Similarly, Scherr et al, 1962, report that their calculations yield only an order of magnitude for the W_3^n and fails completely in the determination of W_4^n for the He isoelectronic sequence (with screening constant), if the relativistic energy contributions are not subtracted off beforehand.

2.8 Applications to nuclear magnetic shielding constants

For a many electron atom or ion, the nuclear magnetic shielding constant σ , is defined as the ratio of the magnitude of the induced shielding field at the nucleus, produced by an external magnetic field to the magnitude of the external field itself. The nuclear magnetic shielding constant thus gives a measure of the diamagnetic shielding of the nucleus by the electrons. In the particular case of an atomic system in a 'S state, Lamb, 1941, derived an expression for σ , showing it to depend on the electron-nuclear potential energy in the following way

$$\sigma = \frac{\alpha^2}{3} \sum_i \left\langle \frac{1}{r_i} \right\rangle \quad (2.8.1)$$

where α is the fine structure constant. Hall, 1961, has shown that this potential energy $\sum_i \left\langle \frac{1}{r_i} \right\rangle$ due to the electrons and the nucleus is given by

$$\sum_i \left\langle \frac{1}{r_i} \right\rangle = z \frac{\partial W}{\partial z} \quad (2.8.2)$$

where W is the non-relativistic energy of the atomic system. Equation (2.8.2) also applies to approximate wave functions, provided they are in a certain ^{sense} stable under the perturbation of a change in z (see Hall, 1961). The simpler relation

$$\sigma = - \frac{\alpha^2}{3} \frac{\partial W}{\partial z} \quad (2.8.3)$$

can therefore be given. The importance of equation (2.8.3) lies in the fact that σ can be deduced from W without any quantum-mechanical calculation. The z^{-1} expansion for the non-relativistic energy is therefore highly suitable for estimating σ from equation (2.8.3). In table 2.8, the magnetic shielding constants, σ , are calculated for a number of atoms and ions from the series for $W^n(z)$ obtained in the previous section from theory and experimental data. These should be more accurate than the values given by Ramsey (1953). Also shown in

this table are theoretical values for σ calculated by Rustgi and Tiwari, 1963, using analytic self-consistent functions of Rothean, Sachs, Weiss, 1960 and by Dickinson, 1950, using Hartree-Fock wave functions together with calculations by Ormand and Matsen, 1959 and Hylleraas and Skavlen, 1950. It may be seen that all the results in table 2.8 are in close agreement. It must however, be emphasized that not all the atomic systems considered in table 2.8 have a ground state denoted by the 'S term, and for such systems σ is tensor-like in form. In that case, σ as given by equation (2.8.1) should be interpreted as the average of the trace of this tensor.

For the most part, the estimates of σ in the literature are obtained using approximate wave functions to calculate $\sum_i \langle \frac{1}{r_i} \rangle$, (see also, part II of this thesis, where $\sum_i \langle \frac{1}{r_i} \rangle$ is calculated for two and three electron systems using density functions.) However, at the present time there appears to be only one other method based on experimental data for the determination of σ (Silverman and Obata, 1963). In their paper, Silverman and Obata define the coherent X-ray scattering amplitude as

Table 2.8

Nuclear Magnetic Shielding Constants

		(σ x 10 ⁵)						
n	z	2	3	4	5	6	7	8
		5.9944	9.5423	13.092				
		5.9938(a)	9.5396(b)	13.091(b)				
2		5.9856(b)	9.4848(c)	13.092(c)				
		6.0021(c)						
		6.0 (d)						
		10.154	14.153	18.149				
		10.138(b)	14.139(b)					
3		10.145(c)	14.151(c)					
		10.1	14.962	19.407	23.848			
			14.914(b)					
4			14.926(c)					
			14.9 (d)					
				20.233	25.127	30.016		
5				19.9(d)				
					26.108	31.449	36.783	
6					26.1(d)			

(a) Hylleraas and Skavlem, 1950.

(b) Ormand and Matsen, 1959.

(c) Rustgi and Tiwari, 1963.

(d) Dickinson, 1950.

$$f(\underline{H}, \beta, \gamma) = \int \rho(\underline{r}) \exp(i\underline{H} \cdot \underline{r}) d\underline{r} \quad (2.8.4)$$

(see for example, James, 1950), where $\underline{H} = \frac{2\pi}{\lambda}(\underline{s} - \underline{s}_0)$, $\underline{s}$ and $\underline{s}_0$ are unit vector along the directions of the diffracted and incident beams, λ is the wave length of the radiation, $\underline{r}$ is a co-ordinate system fixed in space, $\rho(\underline{r})$ is the charge distribution function of the scatterer, and β and $\pi - \gamma$ are the polar and azimuthal angles respectively of $\underline{H}$ referred to a co-ordinate system fixed in the scatterer. They then succeed in showing that for spherically symmetric states

$$\int_0^\infty f(H) dH = \frac{3}{2} (\pi/\alpha^2) \sigma \quad (2.8.5)$$

Now since there exists experimentally determined X-ray scattering factor curves for some atomic systems, (see for example Hanson, 1962), equation (2.8.5) furnishes a useful sum rule to calculate σ . Silverman and Obata demonstrate this method by numerically integrating the X-ray scattering factor curve for Br for most of the range, and estimate the contribution of the unobserved tail using shielded hydrogenic orbitals. Their result for σ $305 \times 10^{-5} H_R$ may be compared with that given by Dickinson, 1950, i.e. $308 \times 10^{-5} H_R$.

2.9 Applications to Correlation Energy.

In the Hartree-Fock treatment of many electron systems, the mutual repulsion between electrons with antiparallel spins is not fully taken into account. The Pauli Principle, however, ensures that account is taken of the main part of the correlation of electrons with parallel spin. Thus, in the calculation of the total energy of the system by the Hartree-Fock approximation, there will result an error, the correlation energy, E_{corr} which is defined by

$$E_{\text{corr}} = E_{\text{NR}} - E_{\text{HF}} \quad (2.9.1)$$

where E_{NR} is the exact non-relativistic energy and E_{HF} is the energy obtained using the Hartree Fock approximation.

The correlation problem is very complicated (see, for example, Löwdin, 1959). In principle there are two ways of determining E_{corr} . One is to calculate both E_{NR} and E_{HF} . However, the calculation of E_{NR} cannot be done with sufficient accuracy at present except for the simplest systems. The alternative is to use experimental values and to subtract off estimates of the relativistic contributions.

At first sight, therefore, the isoelectronic sequence is a powerful method of discussing the

correlation energy, first because it enables the non-relativistic energy to be discussed as a function of z , and secondly because the higher order coefficients of the series may be determined by fitting experimental data. The situation is further improved since the perturbation expansion in z^{-1} can be made for the Hartree-Fock case in precisely the same manner as the usual treatment, remembering, however, the restraint upon the form of wave function as a single determinant (see Linderberg and Shull, 1960). The unperturbed Hamiltonian is again separable and for the zero-order wave function the single Slater determinant composed of Hydrogen atom eigenfunctions is obtained. Thus when nondegenerate perturbation theory applies, W_0 and W_1 of equation (1.2.4) are precisely the values of the zero- and first order energies respectively in the Hartree-Fock expansion. In such a case the correlation energy is approximately independent of z , the remaining dependence being small through the W_3/z term, important only for atoms of low nuclear charge. This dependence may be estimated for a number of simple systems since W_3 in the exact non-relativistic expansion is known, for example from fitting experimental data and W_3 in the Hartree-Fock

expansion has been evaluated by Linderberg, 1961, using perturbation methods for the $1s^2$, $1s^2 2s$, and $1s^2 2s^2$ atomic configurations.

In those situations where degenerate perturbation theory must be used for the exact non-relativistic expansion (see section 1.3), the Hartree-Fock expansion is simpler, since the restriction to a single determinantal wave function removes all considerations of degeneracy. Thus for the case of the configuration $1s^2 2s^2$, ^1S which is degenerate with the configuration $1s^2 2p^2$, ^1S , Linderberg and Shull compute the non-relativistic expansion

$$W_{NR} = -1.25z^2 + 1.559274z \dots, \quad (2.9.2)$$

whereas the Hartree-Fock expansion begins

$$W_{HF} = -1.25z^2 + 1.571001z \dots, \quad (2.9.3)$$

The correlation energy, thus begins with a linear term, $-0.011727z$.

Table 2.9 as given by Linderberg and Shull, 1960 lists the z dependence on correlation energy of a number of systems all having L -shell configurations according to whether the correlation energy is essentially linearly dependent or not on z .

Table 2.9

z Dependence of Correlation Energy for L-Shell
Configurations.

n	Configuration	Correlation energy	
		Linear in z	No linear term in z
2	$1s^2$		^1S
3	$1s^2 2s$		^2S
	$1s^2 2p$		^2P_o
4	$1s^2 2s^2$	^1S	
	$1s^2 2s2p$		$^1P^o, ^3P^o$
	$1s^2 2p^2$	^1S	$^1D, ^3P$
5	$1s^2 2s^2 2p$	^2P_o	
	$1s^2 2s2p^2$		$^2S, ^2P, ^2D, ^4P$
	$1s^2 2p^3$	^2P_o	$^2D^o, ^4S^o$
6	$1s^2 2s^2 2p^2$	$^1S, ^1D, ^3P$	
	$1s^2 2s 2p^3$		$^1P^o, ^1D^o, ^3S^o, ^3D^o, ^5S^o$
	$1s^2 2p^4$	$^1S, ^1D, ^3P$	

PART II

ANALYTICAL CALCULATIONS OF
ATOMIC PROPERTIES

CHAPTER 3

THE DOUBLE PERTURBATION EXPANSION AND THE F FUNCTION TECHNIQUE

3.1 Introduction

The development of isoelectronic sequences of atoms as a perturbation theory has produced a number of important consequences in the study of atomic spectra. Chief amongst these is the possibility of applying the method to investigate atomic properties other than the electronic energy. From the expansion of the wave function, expansions for all the atomic properties may be derived. For many purposes the first few terms in the expansions are sufficiently accurate to determine the major trends throughout the isoelectronic sequence and may even be quantitatively accurate. Thus, even though the original Schrödinger equation cannot be solved analytically, the first few terms in the expansions for various properties can be calculated in closed form. Techniques for finding these closed solutions comprise the content of this chapter.

This use of perturbation theory in the calculation of atomic properties has revived the interesting problem of using existing wave functions more efficiently in calculating such properties. This arises from the fact that for an approximate wave function with error of order η , the error in the total energy is of order η^2 and so is

relatively insensitive to improvements in the wave function, whereas, for most other properties the error is of order η and so is much larger and more sensitive. Since η may be large, even for a function which gives a good total energy, the calculations of other properties fluctuate considerably and do not seem to converge as η is decreased. The usual method recommended for improving the calculations is to improve the wave function by further minimization of the energy. This, in many ways, is unsatisfactory since it evades the real problem. The perturbation study of atomic properties is a much more fundamental approach to the problem, and the method discussed in this chapter leads to calculations of properties in which the errors are of order η^2 .

For the purposes of calculation, atomic (and molecular) properties fall into three classes. The largest class consists of those properties which are defined as the mean value of some operator taken over the exact eigenfunction for some state. Such properties usually arise physically through a small perturbation of the system represented by the perturbing operator and the resulting first order change in energy is just the mean value of the operator. The next class consists of

properties defined in terms of higher order perturbation theory for example polarizabilities and effects due to the combined application of several perturbations. The third class consists of those properties, such as transition probabilities which depend on several states. Part II of this thesis deals exclusively with the first class.

3.2 The double perturbation expansion

The basis of this new method is primarily due to Dalgarno, Lewis and Stewart (Dalgarno and Lewis, 1955; Dalgarno and Stewart, 1956; 1960). Their work was re-formulated and extended by Schwartz (Schwartz, 1959a; 1959b). Some of their results will be discussed in later sections of this chapter. The same fundamental ideas have been applied by these authors using different mathematical techniques which very often tend to obscure the nature of the basic problem. A simpler and much more fundamental mathematical approach used by Hall, 1964, is to formulate the problem in terms of a double perturbation theory.

The Hamiltonian of the system is denoted by H and the perturbing operator is P with the small parameter ε so that the perturbed Hamiltonian is

$$H + \varepsilon P \quad (3.2.1)$$

An expansion in terms of isoelectronic sequences may have, for example, by changing scale

$$\varepsilon = (z - \alpha)^{-1} \quad (3.2.2)$$

The available wave function ϕ is not an eigenfunction of H but it will be assumed that there is a Hamiltonian h for which it is an exact eigenfunction so that

$$h\phi = e_0\phi \quad (3.2.3)$$

and, for convenience, ϕ is normalized to unity. The error can be defined as

$$\eta v = H - h \quad (3.2.4)$$

where v is the operator of the error and η its magnitude. The perturbed Hamiltonian can then be written as

$$h + \eta v + \varepsilon P \quad (3.2.5)$$

and the perturbed eigenfunction and eigenvalue expanded as a double power series in both η and ε . The eigenfunction is, therefore,

$$\psi = \phi + \eta \phi_{01} + \varepsilon \phi_{10} + \eta \varepsilon \phi_{11} + \dots \quad (3.2.6)$$

and the eigenvalue

$$W = e_0 + \eta e_{01} + \varepsilon e_{10} + \eta \varepsilon e_{11} + \dots \quad (3.2.7)$$

From the eigenvalue equation

$$(\hbar + \eta, v + \epsilon P) \psi = W \psi \quad (3.2.8)$$

equations are deduced for the terms of the various orders in the same way as those obtained for a single perturbation expansion as discussed in section 1.2 of this thesis. In particular, the first order energy coefficients are

$$e_0 = \int \phi^* \hbar \phi \, d\tau \quad (3.2.9)$$

$$e_{01} = \int \phi^* v \phi \, d\tau = \langle v \rangle \quad (3.2.10)$$

$$e_{10} = \int \phi^* P \phi \, d\tau = \langle P \rangle \quad (3.2.11)$$

and the bilinear coefficient is

$$e_{11} = \int \{ \phi_{01}^* (P - \langle P \rangle) \phi + \phi^* (P - \langle P \rangle) \phi_{01} \} d\tau \quad (3.2.12)$$

or alternatively

$$e_{11} = \int \{ \phi_{10}^* (v - \langle v \rangle) \phi + \phi^* (v - \langle v \rangle) \phi_{10} \} d\tau \quad (3.2.13)$$

The perturbed wave functions ϕ_{01} and ϕ_{10} are determined by

$$(\hbar - e_0) \phi_{01} = (e_{01} - v) \phi \quad (3.2.14)$$

$$(\hbar - e_0) \phi_{10} = (e_{10} - P) \phi \quad (3.2.15)$$

It is of considerable importance to note that e_{11} can be calculated in two quite different ways depending on whether ϕ_{01} is known and equation (3.2.12) used or ϕ_{10} with equation (3.2.13).

In relation to the original form of the Hamiltonian, the terms in η give the effect of the error in ϕ . The first order change in the energy caused by P becomes

$$W_1 = \left(\frac{\partial W}{\partial \epsilon} \right)_{\epsilon=0} = e_{10} + \eta e_{11} + O(\eta^2) \quad (3.2.16)$$

Thus to obtain an estimate of W_1 whose error is quadratic in η it is necessary to calculate, instead of the customary mean value e_{10} , the more elaborate expression

$$W_1 = e_{10} + \eta e_{11} \quad (3.2.17)$$

The bilinear term e_{11} measures the extent to which the two perturbations interfere with one another. The first order error is, similarly

$$e_{01} + \epsilon e_{11} \quad (3.2.18)$$

and this will vanish for arbitrary ϵ only if both e_{01} and e_{11} vanish.

Although the Hamiltonian h can always be constructed formally by using the projection operator onto ϕ , the subsequent calculations are much simpler if ϕ is such that h can be written down explicitly in operator form. The ground state of the helium atom isoelectronic sequence is an example of this which has been discussed by Dalgarno and Stewart, 1956 and 1960. Corresponding to the wave function

$$\phi = \zeta^3 \pi^{-1} \exp\{-\zeta(r_1 + r_2)\} \quad (3.2.19)$$

the Hamiltonian can be taken as

$$h = \left(-\frac{1}{2} \nabla_1^2 - \zeta/r_1\right) + \left(-\frac{1}{2} \nabla_2^2 - \zeta/r_2\right) \quad (3.2.20)$$

and the error is

$$\eta_v = \frac{1}{r_{12}} - (z - \zeta)/r_1 - (z - \zeta)/r_2 \quad (3.2.21)$$

Because of the presence of the interelectronic repulsion term, the equation for ϕ_{01} cannot be solved in terms of known functions but there is the variational method of solution of Hylleraas, 1930, and the highly accurate series solution of Knight and Scherr, 1962, (see section 2.3). For most perturbations it is easier to solve equation (3.2.15) for ϕ_{10} and use equation (3.2.13) to calculate W_1 . Dalgarno and Stewart, 1956, compare the two methods of calculation and show how the rate of convergence of the series for e_{11} may vary depending on the trial functions used for ϕ_{01} .

Hall, 1964, shows how this method may be extended to include other atoms and even some simple molecules. The Hamiltonian h is taken as the sum of one-electron operators

$$h = \sum_i g(i) \quad (3.2.22)$$

for which spin-orbitals ω_r , defined by the eigenfunction equation

$$g\omega_r = \lambda_r \omega_r \quad (3.2.23)$$

can be found exactly. The hydrogen-like form of g , as in equation (3.2.20) will serve for atoms and even for diatomic hydrides (see part IV of this thesis). If the total energy is non-degenerate the ground state eigenfunction of h has the form of a determinant of the orbitals ω_r . When there is degeneracy, the eigenfunction contains several determinants and the theory becomes much more elaborate. The error operator can still be written down and, if g consists of the usual one-electron kinetic energy operator and some potential terms, ηv will consist of potential terms alone. When the perturbation P has the particular form of a sum of one-electron operators

$$P = \sum_i p(i) \quad (3.2.24)$$

then the μ_r , the first order changes in the orbitals, are determined by

$$(g - \lambda_r)\mu_r = (\lambda'_r - p)\omega_r \quad (3.2.25)$$

where

$$\lambda'_r = \int \omega_r^H p \omega_r d\tau \quad (3.2.26)$$

The perturbed wave function ϕ_{10} has the form of a sum of determinants each having one μ_r replacing a ω_r in the original determinant. If equation (3.2.25) can be solved for the μ_r the value of W_1 is readily obtained in terms of one-electron integrals.

3.3 The F function technique

In his review article, Hall points out that a major disadvantage of the double perturbation treatment described in section 3.2 is that it requires the approximate wave function to be an eigenfunction of some Hamiltonian h and, in practical calculations, needs to know h explicitly in order to calculate the effect of the error. This disadvantage is removed in a modification of the method due to Schwartz, 1959a; 1959b. The essential step in his method is the writing of the perturbed function ϕ_{10} as

$$\phi_{10} = F \phi \quad (3.3.1)$$

where F is a function of the same variables as ϕ .

The perturbation equation is

$$(h - e_0)F\phi = (e_{10} - P)\phi \quad (3.3.2)$$

and, since ϕ is an eigenfunction of h , this becomes

$$(hF - Fh)\phi = (e_{10} - P)\phi \quad (3.3.3)$$

Now if h has the same kinetic energy operator as H and F is a function of the coordinates alone, then their commutators with F are identical

$$[h, F] = hF - Fh = HF - FH = [H, F] \quad (3.3.4)$$

and the equation determining F becomes

$$[F, H]\phi = (E - \langle P \rangle)\phi \quad (3.3.5)$$

The expression for W_1 in terms of F is

$$W_1 = \int \phi^\dagger F \phi \, dT + \int \phi^\dagger \{ F^\dagger (\eta^\dagger v - \eta^\dagger e_{01}) + (\eta^\dagger v - \eta^\dagger e_{01}) F \} \phi \, dT \quad (3.3.6)$$

and the error operator can be eliminated from this by putting

$$\begin{aligned} \int \phi^\dagger F^\dagger (\eta^\dagger v - \eta^\dagger e_{01}) \phi \, dT &= \int \phi^\dagger F^\dagger (H - h - \eta^\dagger e_{01}) \phi \, dT \\ &= \int \phi^\dagger F^\dagger (H - e_0 - \eta^\dagger e_{01}) \phi \, dT \\ &= \int \phi^\dagger F^\dagger (H - \langle H \rangle) \phi \, dT \end{aligned} \quad (3.3.7)$$

where

$$\langle H \rangle = \int \phi^\dagger H \phi \, dT$$

so that

$$W_1 = \int \phi^\dagger P \phi \, dT + \int \phi^\dagger \{ F^\dagger (H - \langle H \rangle) + (H - \langle H \rangle) F \} \phi \, dT \quad (3.3.8)$$

In this method, therefore, no splitting of the original Hamiltonian H is needed either to calculate the perturbed wave function from equation (3.3.5) or the accurate mean value from equation (3.3.8). Equations (3.3.5) and (3.3.8) have been derived directly by Schwartz (1959b) without invoking double perturbation theory but it is extremely difficult to show the order of

magnitude of the error. Hall's derivation of equations (3.3.5) and (3.3.8) thus establishes this technique as exact only to first order and not merely exact to within terms of second order.

Schwartz, 1959b, further discusses three different methods of solving equation (3.3.5). In some especially simple instances a particular integral of the equation can be found by inspection. Alternatively if equation (3.3.5) can be reduced to a number of separate equations each involving one function of one variable then the solution can be written down as an indefinite integral (Young and March, 1958). The difficulties involved in such solutions due to the presence of singularities are discussed by Brown and Hirschfelder, 1963. The solution often involves integrals which are only conditionally convergent and have to be handled with great care (see also Chapter IV). Since the functional

$$J = \int \phi^* \{ F^* (P - \langle P \rangle) + (P - \langle P \rangle) F - \frac{1}{2} F^* [F, H] + \frac{1}{2} [F^*, H] F \} d\tau \quad (3.3.9)$$

is stationary for fixed ϕ when F satisfies equation (3.3.5) and F^* the conjugate equation, the third method of determining F is to assume some parametric form for it

and make J stationary with respect to those parameters. This variation principle is closely related to that used in ordinary perturbation theory (Hylleraas, 1930).

3.4 Results

Dalgarno and Stewart, 1956 and 1960, and Schwartz, 1959b, have applied these methods to calculate a number of properties of the ground state of Helium, Dalgarno and Stewart using the perturbation method and Schwartz the F function technique. The screening procedure as used by Dalgarno and Stewart in the form of equations (3.2.19), (3.2.20) and (3.2.21) define W_1 for each particular perturbation, as a function of ζ . For each operator, W_1 was calculated at the value of ζ chosen so as to minimize the unperturbed energy, and also at the value of ζ chosen to make the wave function stable under the particular perturbation involved. This latter value of ζ varies from perturbation to perturbation and its significance is discussed in Chapter IV. Some illustrative results are given in table 3.1 and are compared with the self-consistent field results and the highly accurate results of Pekaris, 1959. Similar calculations carried out by Schwartz contained errors, and the expressions for W_1 were

not evaluated at stable values of ζ . These errors have been corrected and the results, which have been amended to include screening agree exactly with those obtained by Dalgarno and Stewart. For example, for the diamagnetic susceptibility operator $(r_1^2 + r_2^2)$

$$F = -\frac{1}{3\zeta}(r_1^3 + r_2^3) - \frac{1}{\zeta^2}(r_1^2 + r_2^2) \quad (3.4.1)$$

so that

$$W_1 = \langle r_1^2 + r_2^2 \rangle = \frac{6}{\zeta^2} \left\{ 1 + \frac{2}{\zeta}(\zeta - z) + \frac{51}{64\zeta} \right\} \quad (3.4.2)$$

The expressions for the other results quoted in table 3.4 (in terms of arbitrary z and ζ) with their corresponding F functions are as follows:

$$\langle r_1 + r_2 \rangle = \frac{3}{\zeta} \left[1 + \frac{\zeta - z}{\zeta} + \frac{3}{8\zeta} \right] \quad (3.4.3)$$

and

$$F = -\frac{1}{2\zeta}(r_1^2 + r_2^2) \quad ; \quad (3.4.4)$$

$$\langle r_1^{-1} + r_2^{-1} \rangle = 2\zeta \left[1 - \frac{\zeta - z}{\zeta} - \frac{5}{16\zeta} \right] \quad (3.4.5)$$

and

$$F = (r_1 + r_2) \quad ; \quad (3.4.6)$$

$$4\pi \langle \delta(r_1) + \delta(r_2) \rangle = 8\zeta^3 \left\{ 1 - \frac{2(\zeta - z)}{\zeta} - \frac{19}{16\zeta} + \frac{3}{4\zeta} \ln 2 \right\} \quad (3.4.7)$$

and

$$F = \left[-2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + 4\zeta^2 (r_1 + r_2) + 4\zeta \ln r_1 r_2 \right] \quad (3.4.8)$$

A more extensive table of the positive powers has been calculated by Gordon, 1963 . The X-ray scattering factor has been considered by Weiss, 1963 . Results for the ^3S state of helium and for the lithium ground state are given in chapter IV of this thesis.

Table 3.4

Ground state properties for the helium atom

operator	$\zeta = z^{-5/16}$	at stable ζ	S.C.F.	accurate
$4\pi[S(r_1)+S(r_2)]$	44.591(a)	44.925(a)	45.194(c)	45.501(d)
$r_1 + r_2$	1.844(b)	1.846(b)	1.854(c)	1.859(d)
$r_1^2 + r_2^2$	2.322(a)	2.339(a)	2.369(c)	2.387(d)
$r_1^{-1} + r_2^{-1}$	3.375(a)	3.375(a)		3.377(d)

(a) Dalgarno and Stewart 1960.

(b) Hall et al. 1964.

(c) Roothaan et al. 1964.

(d) Pekeris 1959, 1962.

CHAPTER 4

THE DIRECT CALCULATION OF THE FIRST ORDER DENSITY MATRIX FOR ATOMS

4.1 Introduction

One disadvantage of the F function technique described in Chapter 3 is that, for each new perturbation, a new F function has to be calculated by solving equation (3.3.5). This arises because, in effect, e_{11} is being calculated using equation (3.2.12) instead of equation (3.2.13), the exact solution of equation (3.2.13) being too difficult for the reasons already discussed. However, in his formative paper (1959, a) Schwartz showed that there was also another interesting possibility. This was the direct calculation of the electron density for the helium atom ground state to zero and first orders without knowing the wave function. In view of the current interest in the problem of calculating the density matrix independently of the wave function (e.g. Lowdin, 1955; Coleman, 1963), it is worthy of note that this partial solution of the problem has been already found.

The main purpose of this chapter is to generalize this Schwartz result to include the calculation of the zero and first order perturbation terms for the density matrices of a wide class of atomic and molecular systems. Analytical solutions of the resulting equations are possible using

existing techniques for only a limited number of atomic sequences. Once the density matrix is known the calculation of properties which are expressible as the mean values of one-electron operators becomes relatively easy.

4.2 The first order correction to the density matrix

The Hamiltonian, H , which determines the behaviour of an atom or molecule is divided into two parts

$$H = H_0 + V \quad (4.2.1)$$

where H_0 is the sum of one-electron operators

$$H_0 = \sum_{i=1}^N f_i \quad (4.2.2)$$

and V , the perturbation, can be written as a sum of two-electron terms

$$V = \sum_{i < j}^N g_{ij} \quad (4.2.3)$$

Thus, for an atomic sequence with nuclear charge z ,

$$f_i = -\frac{1}{2} \nabla_i^2 - (z-\alpha)/r_i \quad (4.2.4)$$

$$g_{ij} = -\alpha/(N-1)r_i - \alpha/(N-1)r_j + 1/r_{ij} \quad (4.2.5)$$

where α is a screening constant which can be fixed later.

The eigenfunction of H is expressed as a series in the

parameter ϵ which is determined by the way in which the Hamiltonian is divided

$$\bar{\Psi} = \bar{\Psi}_0 + \epsilon \bar{\Psi}_1 + \epsilon^2 \bar{\Psi}_2 + \dots \quad (4.2.6)$$

The atomic sequences, for example, may have, by changing scale

$$\epsilon = (z - \alpha)^{-1} \quad (4.2.7)$$

or ϵ may be regarded as a formal parameter and put equal to unity.

Because of the form of H_0 as a sum of one-electron operators, the zero-order eigenvalue equation separates into orbital equations and the zero-order wave function in the absence of degeneracy is a determinant of these spin-orbitals

$$\bar{\Psi}_0 = (N!)^{-\frac{1}{2}} \text{Det}\{\psi_1(1), \psi_2(2), \dots, \psi_N(N)\} \quad (4.2.8)$$

where the orbitals satisfy

$$f_i \psi_k(i) = e_k \psi_k(i) \quad (4.2.9)$$

and

$$W_0 = \sum_{k=1}^N e_k \quad (4.2.10)$$

When W_0 is degenerate, $\bar{\Psi}_0$ is a linear combination of similar determinants and the remaining parts of the argument do not apply.

Since the set of all such determinants forms a complete set of functions for antisymmetric functions of N

electrons, the first order correction to the wave function can be expanded in the series

$$\bar{\Psi}_1 = \sum_{\underline{n}} c_{\underline{n}} \bar{\Phi}_{\underline{n}} \quad (4.2.11)$$

where

$$\bar{\Phi}_{\underline{n}} = (N!)^{-\frac{1}{2}} \text{Det}\{\psi_{n1}(1), \psi_{n2}(2), \dots, \psi_{nN}(N)\} \quad (4.2.12)$$

and all the various orbitals are solutions of the orbital equation

$$f\psi_k = e_k \psi_k \quad (4.2.13)$$

It is convenient to restrict the terms in equation (4.2.11) to those determinants which cannot be turned into one another by some permutation of the subscripts $\underline{n}$. The perturbation equation which determines $\bar{\Psi}_1$, is easily solved in this expansion and the coefficients are given by

$$c_{\underline{n}} = (W_0 - W_{\underline{n}})^{-1} \int \bar{\Phi}_{\underline{n}}^* V \bar{\Phi}_0 d\tau \quad (4.2.14)$$

$$c_0 = 0$$

where

$$W_{\underline{n}} = \sum_{r=1}^N e_{nr} \quad (4.2.15)$$

The choice of c_0 as zero ensures that the first order wave function is orthogonal to the zero order one. By integrating over the coordinates of $(N-2)$ electrons, the coefficients can be expressed in the simpler form

$$c_{\underline{n}} = (W_0 - W_{\underline{n}})^{-1} \left(\prod_{t=1}^N \delta_{n_t, t} \right) \int \{ \psi_{n_1}^*(1) \psi_{n_j}^*(2) - \psi_{n_j}^*(1) \psi_{n_1}^*(2) \} \varepsilon_{12} \psi_i(1) \psi_j(2) d\tau_{12} \quad (4.2.16)$$

where the double prime indicates that the terms with $t = i$ and $t = j$ are to be omitted from the product. The Kronecker deltas imply that $c_{\underline{n}}$ vanishes when the corresponding determinant differs from $\bar{\Psi}_0$ in respect of more than two orbitals. The sign of $c_{\underline{n}}$ implies that the orbitals common to $\bar{\Psi}_0$ and $\bar{\Phi}_{\underline{n}}$ appear in the same positions in both determinants.

The first-order density matrix is defined as

$$\gamma(1/1') = N \int \bar{\Psi}^*(1,2,\dots) \bar{\Psi}(1',2,\dots) d\tau_2 \dots d\tau_N \quad (4.2.17)$$

and, when the wave function is expanded, the zero-order term in the density matrix expansion becomes

$$\gamma_0(1/1') = \sum_r^N \psi_r^*(1) \psi_r(1') \quad (4.2.18)$$

while the first-order term becomes

$$\begin{aligned} \gamma_1(1/1') = & N \sum_{\underline{n}} c_{\underline{n}} \int \bar{\Phi}_{\underline{n}}^*(1,2,\dots) \bar{\Psi}_0(1',2,\dots) d\tau_2 \dots d\tau_N \\ & + N \sum_{\underline{n}} c_{\underline{n}} \int \bar{\Psi}_0^*(1,2,\dots) \bar{\Phi}_{\underline{n}}(1',2,\dots) d\tau_2 \dots d\tau_N \end{aligned} \quad (4.2.19)$$

Because of the orthogonality of the orbitals, the only terms in the series which will contribute to this expression will have $\bar{\Phi}_{\underline{n}}$ which differ from $\bar{\Psi}_0$ in respect to only one orbital. It is convenient now to re-label the coefficient

$c_{\underline{n}}$, of a term in which the orbital ψ_r replaces an orbital ψ_s of $\bar{\psi}_0$ as c_{rs} so that

$$\chi_1(1/1') = \sum_{r=N+1}^{\infty} \sum_{s=1}^N \{c_{rs}^* \psi_r^*(1) \psi_s(1') + c_{rs} \psi_s^*(1) \psi_r(1')\} \quad (4.2.20)$$

and, from equation (4.2.16)

$$c_{rs} = (W_0 - W_{rs})^{-1} \sum_{t \neq s}^N \int \{ \psi_r^*(1) \psi_t^*(2) - \psi_t^*(1) \psi_r^*(2) \} g_{12} \psi_s(1) \psi_t(2) dT_{12} \quad (4.2.21)$$

Because of the orbital equations (4.2.13),

$$W_0 - W_{rs} = e_s - e_r \quad (4.2.22)$$

At this point we introduce a set of N functions F_s as solutions of the equations

$$\begin{aligned} (fF_s - F_s f) \psi_s &= [f, F_s] \psi_s(1) \\ &= \sum_{t \neq s}^N \psi_t(1) \int \psi_t^*(2) g_{12} \psi_s(2) dT_2 \\ &\quad - \psi_s(1) \sum_{t \neq s}^N \int \psi_t^*(2) g_{12} \psi_t(2) dT_2 + K_s \psi_s(1) \end{aligned} \quad (4.2.23)$$

where $K_s \psi_s(1)$ is a multiple of the solution of the homogeneous equation, and note that, if these equations can be solved, the integral

$$\int \psi_r^* [f, F_s] \psi_s dT = - (e_s - e_r) c_{rs}, \quad (4.2.24)$$

but

$$\int \psi_r^* (f F_s - F_s f) \psi_s d\tau = (e_r - e_s) \int \psi_r^* F_s \psi_s d\tau$$

so that

$$c_{rs} = \int \psi_r^* F_s \psi_s d\tau, \quad s \leq N < r \quad (4.2.25)$$

Since the integral in (4.2.24) vanishes when $r = s$ the left side of equation (4.2.23) must vanish when multiplied by ψ_s^* and integrated. This condition which is necessary for the solubility of equation (4.2.23), fixes the value of the constant K_s as

$$K_s = \sum_{t \neq s} L_{st}; \quad (4.2.26)$$

$$L_{ts} = L_{st} = \int \psi_s^*(1) \psi_t^*(2) g_{12} \{ \psi_s(1) \psi_t(2) - \psi_t(1) \psi_s(2) \} d\tau_2$$

Alternatively, equation (4.2.23) can be written as

$$[f, F_s] \psi_s = \sum_{t \neq s} \psi_t \int \psi_t^* (g_{12} - L_{st}) \psi_s d\tau$$

$$- \psi_s \sum_{t \neq s} \int \psi_t^* (g_{12} - L_{st}) \psi_t d\tau \quad (4.2.27)$$

Since the eigenfunctions of f form a complete set of functions the product $F_s \psi_s$ can be expanded as

$$F_s \psi_s = \sum_{r=1}^{\infty} a_{rs} \psi_r \quad (4.2.28)$$

where

$$\begin{aligned} a_{rs} &= \int \psi_r^* F_s \psi_s d\tau \\ &= c_{rs} \quad \text{for } r > N \end{aligned} \quad (4.2.29)$$

so that, since c_{rs} is not defined for $r \leq N$,

$$F_s \psi_s = \sum_{r=1}^N a_{rs} \psi_r + \sum_{r=N+1}^{\infty} c_{rs} \psi_r \quad (4.2.30)$$

Furthermore, using equation (4.2.27)

$$\begin{aligned} a_{rs} = (e_r - e_s)^{-1} \sum_t \int \psi_r^*(1) \psi_t^*(2) (g_{12} - L_{st}) \{ \psi_t(1) \psi_s(2) \\ - \psi_s(1) \psi_t(2) \} d\tau_{12}, (r \neq s) \end{aligned} \quad (4.2.31)$$

and, hence, it follows that

$$a_{sr} = -a_{rs}^*, \quad (r \neq s) \quad (4.2.32)$$

The expansion (4.2.30) enables the density matrix (4.2.20)

to be put into the closed form

$$\begin{aligned} \gamma_i(1/1') &= \sum_{s=1}^N \{ (F_s^* \psi_s^*(1) - \sum_{r=1}^N a_{rs}^* \psi_r(1)) \psi_s(1') \\ &\quad + \psi_s^*(1) (F_s \psi_s(1') - \sum_{r=1}^N a_{rs} \psi_r(1')) \} \\ &= \sum_{s=1}^N \{ F_s^*(1) - a_{ss}^* + F_s(1') - a_{ss} \} \psi_s^*(1) \psi_s(1') \end{aligned} \quad (4.2.33)$$

using equation (4.2.32). If, as will often happen, both the operators f_i and g_{ij} are independent of spin then the spin orbital will factorize into a spatial orbital and a

spin function. This factorization simplifies the equations above since it results in F_s being a spatial function and in the vanishing of a_{rs} between functions of opposite spin.

4.3 The helium ground state

The ground state of the helium isoelectronic sequence gives a particularly simple illustration of the theory. For this system the operator f is

$$f = -\frac{1}{2} \nabla^2 - (z - \alpha)/r \quad (4.3.1)$$

which is the Hamiltonian for a hydrogen atom with charge $(z-\alpha)$ so that its eigenfunctions are well-known. In particular, the zero-order density matrix, when integrated over spin, is

$$\rho_0(1/2) = (z-\alpha)^3 \pi^{-1} \exp\{-(z-\alpha)(r_1 + r_2)\} \quad (4.3.2)$$

The perturbation is

$$g_{12} = \frac{1}{r_{12}} - \frac{\alpha}{r_1} - \frac{\alpha}{r_2} \quad (4.3.3)$$

Although there are two orbitals the factorization of spin leaves the equations for their F_s functions identical so that the F_s can be taken as equal. Because of the spherical symmetry of the orbital the equation for F can be reduced to a one-variable equation and solved by repeated integration (Young and March, 1958). The lower

limits in these integrations are taken as the origin so that $F(0)$ vanishes. The solution[†] is

$$\xi F(r) = (-8\alpha+5)y/8 - \frac{1}{8} - \frac{1}{4}e^{-2y} - \frac{3}{16}(e^{-2y}-1)/y + \frac{3}{8} \int_0^y \frac{e^{-2x}-1}{x} dx \quad (4.3.4)$$

where

$$\zeta = z - \alpha \quad (4.3.5)$$

$$y = (z-\alpha)r \quad (4.3.6)$$

and using this and equation (4.2.33) the first-order density matrix is

$$\gamma_i(1/2) = \gamma_c(1/2) [F(r_1) + F(r_2) - 2\langle F \rangle] \quad (4.3.7)$$

where the constant term is found to be

$$\langle F \rangle = (-24\alpha + 15)/16\zeta - \frac{11}{32\zeta} - \frac{3}{8\zeta} \ln 2 \quad (4.3.8)$$

This result is a generalization of the electron density calculated by Schwartz, 1959 for the same sequence.

The significance of the first order density matrix is that it enables the mean value of any one-electron operator to be evaluated by an integration. By using the first two terms in its expansion the first two terms in the expansion of the mean values is found directly. This may

[†] Since the integrals appearing in $F(r)$, and in subsequent integrations over $F(r)$ are only conditionally convergent it is essential that the terms be kept grouped together as given here.

be compared with the calculation of these two terms for a number of mean values by Dalgarno and Stewart, 1960 by solving the different perturbation equations for each perturbation as discussed in Chapter III. The advantage of the method used here is that all the mean values are found by solving only one equations. Their results are, of course, identical with ours and have already been discussed in Chapter III. Determined by either method, the mean values depend on α as an undetermined parameter. The best value of α is found by making the mean value stationary with respect to α . This has the natural significance of being the value for which the result is least sensitive to the errors in the zero order wave function. It is also the value which makes the wave function stable (Hall, 1961) in the sense that the contribution to the mean value from the first order term in the density matrix vanishes. The mean value can then be calculated from the zero order term in the density matrix alone but with the scale factor (i.e. α) chosen so as to make the correction vanish. This stable value of α varies from perturbation to perturbation and, in particular, is different from the

value which minimizes the energy. The effect on the mean values can be illustrated from the mean value of r for helium. For the stable α this mean value is 1.846 as compared with 1.844 when α minimizes the energy and 1.859 for the accurate value (Pekeris, 1959).

4.4 The lowest helium triplet state

The component with $S_z = 1$ for the lowest triplet state $(1s, 2s)^3S$, of the helium sequence can be described by a wave function which is a single determinant to zero order in the perturbation. There are two spatial orbitals

$$\psi_1 = (z-\alpha)^{3/2} \pi^{-\frac{1}{2}} \exp\{-(z-\alpha)r\} \quad (4.4.1)$$

$$\psi_2 = (z-\alpha)^{3/2} (32\pi)^{-\frac{1}{2}} \{2-(z-\alpha)\} \exp\{-\frac{1}{2}(z-\alpha)r\} \quad (4.4.2)$$

and two functions F_1 and F_2 corresponding to them. The equations determining F_1 and F_2 can be reduced to one variable equation and hence solved giving

$$\begin{aligned} \zeta F_1(r) = & (-\alpha + \frac{137}{729})y + \frac{296}{729}(1-e^{-y})/y + \frac{592}{729} \int_0^y (e^{-x}-1)/x \, dx \\ & + \frac{8}{81}\alpha(y-2)e^{\frac{1}{2}y} + (-\frac{5}{108}y^2 - \frac{10}{27}y - \frac{97}{81})e^{-y} + \frac{577}{729} + \frac{16}{81}\alpha \end{aligned} \quad (4.4.3)$$

$$\begin{aligned} \zeta_{F_2}(r) = & \frac{362}{729} \int_0^y (e^{-2x}-1)/x \, dx + \frac{181}{729}(1-e^{-2y})/y + \frac{274}{729}y + \frac{189}{729}e^{-2y} \\ & + \frac{115}{729} + \frac{191}{729}(2-y)^{-1} - \frac{1523}{729}e^{-2y}/(2-y) \quad (4.4.4) \\ & - \alpha \left[\frac{1}{2}y + \frac{2}{2-y} - \frac{256}{81} e^{-\frac{1}{2}y}/(2-y) + \frac{47}{81} \right] \end{aligned}$$

By integrating over these functions, the values of the remaining constants are found

$$a_{11} = \int \psi_{F, \psi}^* dT = -\frac{211}{162} \frac{\alpha}{\zeta} + \frac{1399}{4374} \frac{1}{\zeta} - \frac{592}{729} \ln \frac{3}{2} \frac{1}{\zeta} \quad (4.4.5)$$

$$a_{21} = \int \psi_{F, \psi}^* dT = 0 \quad (4.4.6)$$

$$a_{22} = \int \psi_{F_2 \psi_2}^* dT = -\frac{499}{162} \frac{\alpha}{\zeta} + \frac{3208}{2187} \frac{1}{\zeta} - \frac{362}{729} \ln 3 \frac{1}{\zeta} \quad (4.4.7)$$

$$a_{12} = \int \psi_{F_2 \psi_2}^* dT = 0 \quad (4.4.8)$$

and hence the first order term in the density matrix by substitution into equation (4.2.33).

The results of calculations of some mean values are shown in table (4.4)⁺. For each operator the mean value is evaluated for the value of α which minimizes the total energy viz.

$$\alpha_0 = 0.30068587 \quad (4.4.9)$$

⁺Weiss, 1963, obtains a value $\langle \delta(r_1) + \delta(r_2) \rangle = 33.16$ using only a product wave function. In the light of the present calculation, this close agreement with the Pekeris result must be fortuitous, and not indicative of the actual accuracy of the method.

and also at the value of α which makes the wave function stable under that particular perturbation. The accurate values are quoted from the variational calculation of Pekeris (1959). The formulae for arbitrary z and α are given in section (4.6).

Table 4.4 Mean values of some operators for the Helium ^3S state.

Operator	using α_e	stable α	accurate
$4\pi[\delta(r_1) + \delta(r_2)]$	31.3608	32.7212	33.1846
$r_1^{-1} + r_2^{-1}$	2.3121	2.3121	2.3093
$r_1 + r_2$	4.7753	4.8076	5.1009
$r_1^2 + r_2^2$	19.3288	20.1310	22.9286

4.5 The lithium ground state

The ground state of the three-electron isoelectronic sequence has the configuration $(1s)^2 (2s)^2 S$ and so can also be described to zero order using a single determinant of hydrogen-like orbitals. There are three spin orbitals.

$$\psi_1 = (1s)\alpha, \quad \psi_2 = (1s)\beta, \quad \psi_3 = (2s)\alpha \quad (4.5.1)$$

and hence three functions F_1, F_2, F_3 . The equations for these functions simplify on integrating over spin and reduce to

$$\begin{aligned} [f, F_1](1s) &= (2s) \int (2s)^* (g_{12} - L_{13})(1s) d\tau \\ &- (1s) \int (2s)^* (g_{12} - L_{13})(2s) d\tau \\ &- (1s) \int (1s)^* (g_{12} - L_{12})(1s) d\tau . \end{aligned} \quad (4.5.2)$$

$$\begin{aligned} [f, F_2](1s) &= - (1s) \int (1s)^* (g_{12} - L_{12})(1s) d\tau \\ &- (1s) \int (2s)^* (g_{12} - L_{23})(2s) d\tau \end{aligned} \quad (4.5.3)$$

$$\begin{aligned} [f, F_3](2s) &= - (2s) \int (1s)^* (g_{12} - L_{13})(1s) d\tau \\ &+ (1s) \int (1s)^* (g_{12} - L_{13})(2s) d\tau \\ &- (2s) \int (1s)^* (g_{12} - L_{23})(1s) d\tau . \end{aligned} \quad (4.5.4)$$

where the first two hydrogen-like orbitals with effective charge ζ are denoted by (4.4.1) and (4.4.2). The solution of these equations is greatly simplified by noting that many of the terms on the right are of the same form as in the equations already solved so that the solutions are the sum of functions already found with a few additional ones. Allowance has also to be made for the fact that this sequence has

$$g_{ij} = 1/r_{ij} - \alpha/(2r_i) - \alpha/(2r_j) \quad (4.5.5)$$

The solutions are

$$\begin{aligned} \zeta_{F_1} = & (-4\alpha+5)y/8 - \frac{1}{8} - e^{-2y}/4 - 3(e^{-2y}-1)/(16y) \\ & + 3 \int_0^y (e^{-2x}-1)/(8x) dx + (-\frac{1}{2}\alpha + \frac{137}{729})y + \frac{296}{729}(1-e^{-y})/y \\ & + \frac{592}{729} \int_0^y (e^{-x}-1)/x dx + \frac{4\alpha}{81}(y-2)e^{1/2y} \quad (4.5.6) \\ & + (-\frac{5}{108}y^2 - \frac{10}{27}y - \frac{97}{81})e^{-y} + \frac{577}{729} + \frac{8\alpha}{81} \end{aligned}$$

$$\begin{aligned} \zeta_{F_2} = & (-4\alpha+5)y/8 - \frac{1}{8} - e^{-2y}/4 - 3(e^{-2y}-1)/(16y) + \\ & + 3 \int_0^y (e^{-2x}-1)/(8x) dx + \\ & + (\frac{17}{81} - \frac{\alpha}{2})y + [\frac{67}{81} + e^{-y}(-\frac{1}{12}y^2 - \frac{4}{9}y - \frac{11}{9})] \quad (4.5.7) \\ & + \frac{32}{81}(1 - e^{-y})/y + \frac{64}{81} \int_0^y (e^{-x}-1)/x dx \end{aligned}$$

$$\begin{aligned} \zeta_{F_3} = & \frac{362}{729} \int_0^y (e^{-2x}-1)/x dx + \frac{181}{729}(1-e^{-2y})/y + \frac{274}{729}y + \frac{189}{729}e^{-2y} \\ & + \frac{115}{729} + \frac{191}{729} \frac{1}{(2-y)} - \frac{1523}{729} \frac{e^{-2y}}{(2-y)} \\ & - \alpha [\frac{1}{4}y + \frac{1}{(2-y)} - \frac{128}{81} \frac{e^{-\frac{1}{2}y}}{(2-y)} + \frac{47}{162}] \\ & - \frac{\alpha}{2}(\frac{1}{2}y-1) - \frac{\alpha}{(2-y)} + \frac{34}{81}y - \frac{e^{-2y}}{3} - \frac{53}{81} + \frac{71}{81} \frac{1}{(2-y)} \quad (4.5.8) \\ & + \frac{37}{81} \frac{e^{-2y}}{(2-y)} + \frac{13}{81}(1-e^{-2y})/y + \frac{26}{81} \int_0^y (e^{-2x}-1)/x dx \end{aligned}$$

The non-vanishing constants obtained from these functions are

$$a_{11} = \zeta^{-1} \left[-\frac{227}{162} \alpha - \frac{592}{729} \ln \frac{3}{2} - \frac{8}{3} \ln 2 + \frac{1399}{4374} + \frac{19}{32} \right] \quad (4.5.9)$$

$$a_{22} = \zeta^{-1} \left[-\frac{3}{2} \alpha - \frac{64}{81} \ln \frac{3}{2} - \frac{8}{3} \ln 2 + \frac{57}{162} + \frac{19}{32} \right] \quad (4.5.10)$$

$$a_{13} = -a_{31} = \zeta^{-1} \left[-\frac{16\sqrt{2}\alpha}{81} + \frac{2^{16}}{71\sqrt{2.81}} \right] \quad (4.5.11)$$

$$a_{33} = \zeta^{-1} \left[-\frac{371}{162} \alpha - \frac{596}{729} \ln 3 + \frac{5584}{2187} \right] \quad (4.5.12)$$

The relation between a_{13} and a_{31} is used to check the calculation of F_1 and F_3 .

The results for a number of mean values calculated using the density matrix derived from these solutions are shown in Table (4.5). The results are compared with the analytical results obtained by Cohen and Dalgarno, 1963, by solving the restricted Hartree-Fock equations to first order. The value of α which minimizes the energy is

$$\alpha_e = 0.4548009 \quad (4.5.13)$$

Table 4.5 Mean values of operators for
the lithium ground state

operator	α_0	stable α	Cohen and Dalgarno
$4\pi\delta(r)$	56.2719	56.9607	57.734
r^{-1}	1.9065	1.9065	1.909
r	1.4118	1.4693	1.520
r^2	3.7841	4.5859	4.787

4.6 Formulae for arbitrary z and α

For the ^3S state of the helium isoelectronic sequence the expressions for the mean values of various operators to first order are

$$4\pi \langle \delta(r_1) + \delta(r_2) \rangle = -9\zeta^2 + \frac{27z}{2} \zeta^2 + \left[\frac{4736}{729} \ln \frac{3}{2} + \frac{362}{729} \ln 3 - \frac{8804}{2187} \right] \zeta^2$$

$$\langle r_1^{-1} + r_2^{-1} \rangle = \frac{5}{4} z - \frac{137}{729} \quad (\text{independent of } \alpha)$$

$$\langle r_1 + r_2 \rangle = 15\zeta^{-1} - \frac{15z}{2} \zeta^{-2} + \frac{4811}{1458} \zeta^{-2}$$

$$\langle r_1^2 + r_2^2 \rangle = 135\zeta^{-2} - 90z\zeta^{-3} + \frac{8049574}{729 \cdot 243} \zeta^{-3}$$

Similarly, for the $2S$ ground state of the lithium sequence

$$4\pi\langle\delta(r)\rangle = -\frac{17}{3}\zeta^3 + \frac{17z}{2}\zeta^2 + \left[\frac{9940}{2187}\ln 3 - \frac{4970}{2187}\ln 2 + \frac{256}{243} - \frac{90049}{18.729}\right]\zeta^2$$

$$\langle r^{-1} \rangle = \frac{3z}{4} - \frac{5965}{17496}$$

$$\langle r \rangle = 6\zeta^{-1} - 3z\zeta^{-2} + \frac{50297}{24.729}\zeta^{-2}$$

$$\langle r^2 \rangle = 48\zeta^{-2} - 32z\zeta^{-3} + \frac{51}{32}\zeta^{-3} + \frac{18406108}{(729)^2}\zeta^{-3}$$

4.7 Relation between natural and self-consistent orbitals

The natural orbitals of an electronic system have been defined as the orbitals which are eigenfunctions of the density matrix (Lowdin, 1955). It is interesting to ask whether they can be estimated from the expansion of the density matrix found above. This expansion has the form, to the first order

$$\chi(1/2) = \sum_s^N \psi_s^*(1) \psi_s(2) + \sum_s^N \{\phi_s^*(1) \psi_s(2) + \psi_s^*(1) \phi_s(2)\} \quad (4.7.1)$$

where

$$\phi_s = F_s \psi_s - \sum_{r \neq s}^N a_{rs} \psi_r \quad (4.7.2)$$

Clearly, this can be expressed, to the same order of accuracy, as

$$\gamma(1/2) = \sum_s^N [\psi_s^*(1) + \phi_s^*(1)][\psi_s(2) + \phi_s(2)] \quad (4.7.3)$$

and since this is in diagonal form the natural spin orbitals are

$$\psi_s + \phi_s \quad (4.7.4)$$

and their occupation numbers are each unity. From these unit occupation numbers it can be deduced (Lowdin, 1955) that the wave function must be a single determinant and the natural orbitals identical with the self-consistent orbitals or with some unitary transformation of them. The orbitals ϕ_s , therefore, can be recognized as the first order correction to the self-consistent orbital which has ψ_s as its zero-order form. This close relation between the natural orbitals and the self-consistent orbitals is the generalization of the relation between their energies already discovered for the helium and hydrogen molecule ground states (Shull and Lowdin, 1955; Lowdin and Shull, 1956; Shull and Lowdin, 1959; Davidson, 1962). Nazarovoff and Hirschfelder, 1963, have discussed the ground state wave functions of these two-electron systems in more detail and show that the orbitals begin to differ when the perturbation theory is carried to second order and that their energies begin to differ in fourth order.

This theorem enables the result obtained above to be checked by comparison with existing unrestricted Hartree-Fock calculations. The lowest triplet of helium has been treated by Sharma and Coulson, 1962, and from their results for the energy the mean value of r^{-1} can be deduced by differentiation with respect to z using equation (2.8.2). Although their orbitals have the form of infinite series this mean value is identical with that reported in Table 4.5. Similarly, the mean value of r^{-1} for the ground state of lithium calculated from the unrestricted Hartree-Fock energy of Sharma, 1962, agrees with that reported in Table 4.5. The expression for the spin density as a function of z given in closed form by Cohen and Dalgarno, 1963, using the unrestricted Hartree-Fock theory is also identical with the expression deduced from the present theory.

It is convenient to summarize the restrictions involved in this theory by restating the general result in more precise terms. It is assumed that the Hamiltonian can be divided into a main term and a perturbation so that the exact eigenfunction of the main term is a single determinant which also satisfies the Pauli Principle and

is an eigenfunction of the other commuting invariant operators of the system such as the symmetry or the components of angular momentum. The zero-order energy must be non-degenerate but this may sometimes be relaxed if a unique eigenfunction can be found using some of these other operators in addition to the energy. It then follows that the first N natural spin-orbitals of the exact wave function will be identical with the self-consistent spin-orbitals of the system (to within a unitary transformation) to the first order in the magnitude of the perturbation. As can be seen from the lithium example, the self-consistent spin-orbitals have no restriction to double occupation and so are the unrestricted (or spin-polarized) orbitals.

4.8 Discussion and Conclusions

It is important to note that the methods discussed in Part II of this thesis are accurate to terms of first order, and that irrespective of whether double perturbation theory, or the F function technique, or the density matrix method is used the same results are obtained. A further point to note is that effectively each method depends on the

solution of certain differential equations for which closed form solutions may be found. It is interesting to note the renewed attention paid to the differential equations themselves rather than to their formal solutions. (see for example equation (1.3.9)). In this context, the first order agreement with the unrestricted Hartree-Fock calculations of Cohen, 1963, for the 1s, 2s, 2p atomic orbitals, shows that it is possible to find the first order density matrix for a variety of atomic states containing these orbitals provided, of course, the restrictive conditions involved in this theory are satisfied.

Schwartz, 1959b, has succeeded in generalizing the F function technique to second-order calculations. Although, it is difficult to assess the order of magnitude of the error involved in his derivations, one might expect that it would be possible to extend the theory discussed in Chapter III to calculate atomic properties to second order accuracy.

Hall, 1964, remarks that the technique of transforming a function by multiplying it by an F function might be compared with two other important types of functional transformation. First, the transformation of the function by differentiation produces the hypervirial operators

investigated by Hirschfelder and his associates (Hirschfelder, 1960; Epstein and Hirschfelder, 1961; Hirschfelder and Coulson, 1962). Second, the more general transformation is obtained by integrating the function over a kernel. The kernel in the context of equations (3.2.14) and (3.2.15) is the Green's function for the Hamiltonian h and the solution of these equations is the integral over this Green's function multiplied by the terms on the right of the equation. Hall further points out that the existence of all the analytical solutions obtained so far can be traced to the fact that a Green's function can be found in convenient form for the spherically symmetric states of the hydrogen atom.

One final point to make is that much of what is discussed in Part II could be applied to small molecules especially diatomic hydrides. The remaining chapters of this thesis are devoted to extending perturbation theory to investigate the total energy and associated properties of hydride molecules. It might even be possible to investigate the first order density matrix for some simple diatomic molecules, though there is the added complication of its dependence on the internuclear distance.

PART III

THE ELECTRONIC STRUCTURE OF
DIATOMIC HYDRIDES - A UNITED ATOM
APPROACH

CHAPTER 5

UNITED ATOM THEORY AND THE PLATT ELECTROSTATIC MODEL OF DIATOMIC HYDRIDES

5.1 Introduction

Parts I and II of this thesis have been concerned with the electronic structure of atoms. At this juncture, therefore, it becomes reasonable to ask whether or not some of the basic concepts of the previous discussion can be extended to provide a quantum mechanical description of molecules. A method which preserves some of the simpler features of the theory as applied to atoms and which enables the electronic structure of molecules to be discussed is known as 'united atom' theory. United atom theory has a long history and was first used qualitatively in classifying molecular electronic energy levels by Wigner and Witmer, 1928 and qualitatively in the determination of the energy levels of H_2^+ by Morse and Stueckelberg, 1929. This approach has the direct advantage that it is able to utilize the wealth of detailed theoretical calculations and also the large amount of experimental data available for atoms in molecular calculations.

Chapter 5 of this thesis consists of an account of united atom theory together with a brief review of its applications particularly to diatomic hydrides. A

detailed discussion is then given of the Platt electrostatic model of diatomic hydrides (Platt, 1950), while the following Chapter modifies Platt's treatment in order to overcome some of the objections raised by Clinton, 1960.

5.2 The Non-Relativistic Molecular Hamiltonian.

A molecule may be defined as a system of atomic nuclei and electrons, and as such has a non-relativistic Hamiltonian

$$\begin{aligned} \mathcal{H} = & \sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 + \sum_{\alpha < \beta} \frac{z_{\alpha} z_{\beta}}{r_{\alpha\beta}} \\ & - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{\alpha} \sum_i \frac{z_{\alpha}}{r_{i\alpha}} + \sum_{i < j} \frac{1}{r_{ij}} \end{aligned} \quad (5.2.1)$$

where Greek suffices refer to the nuclei and italics to the electrons. z_{α} and M_{α} therefore denote the charge and mass respectively of the nucleus with position coordinate $\underline{r}_{\alpha}$, and $r_{i\alpha}$ is the distance between the nucleus and the i^{th} electron. The units in this Hamiltonian are the usual reduced Hartree units.

Now according to the Born-Oppenheimer approximation, the nuclear and electronic motions in this Hamiltonian may be considered separable (Born-Oppenheimer, 1927).

That is to say, if a solution of the Schrodinger equation of the system is sought such that it is a product of two functions, one of which is a function of nuclear coordinates only and the other is a function of electronic co-ordinates with nuclear co-ordinates regarded as parameters, then the wave equation may be approximately reduced to two equations, one involving the nuclear motion and the other involving the motion of the electrons, provided that the ratio of the electronic mass to the nuclear mass is assumed small. It is with the solution of the wave equation for the electronic motion that the theory of the electronic structure of molecules must commence, since it determines the structure and energy levels of the molecules, and is therefore chemically the most important. The electronic structure of the molecule is therefore governed by the Hamiltonian (in H_R units)

$$H = -\frac{1}{2} \sum_L \nabla_L^2 + \sum_{i < j} \frac{1}{r_{ij}} - \sum_{i, \alpha} \frac{Z_\alpha}{r_{i\alpha}} \quad (5.2.2)$$

This Hamiltonian suggest the physical implication that the nuclei are fixed in known positions while the electrons move in the field of the fixed nuclei.

5.3 United Atom Theory

The 'electronic Hamiltonian' given by 5.2.2 is similar to the non-relativistic Hamiltonian for an atomic system but is more complex, owing to the presence of the more complicated nuclear-potential energy term. The solution of the molecular Schrödinger equation determined by 5.2.2 therefore, is, in general, more difficult than the analogous problem for an atom. As a result, a number of different mathematical techniques of studying the many electron problem in the molecule have been developed. These techniques depend largely on the different ways in which a molecule may be regarded as being built up.

First, from a physical point of view, the molecule may be constructed by adding the individual electrons one after another to the nuclei, an analogous procedure to that used for atoms. Mathematically this involves the theory of vector coupling. Secondly the molecule may be built up by bringing together the atoms of which it consists. From a mathematical point of view the molecule may be regarded as a perturbed system of separated atoms. This approach has led to the well-known valence-bond theory and is responsible for the

linear combinations of atomic orbitals (L.C.A.O) approximation in the molecular orbital (M.O) theory. The third approach characterizes united atom theory in which the building up process starts with zero nuclear separation instead of starting with infinitely large separation. This procedure, often referred to as splitting the so-called 'united atom', is, of course, purely hypothetical but, nevertheless, is extremely useful. In actual fact, a molecule occupies an intermediate position between the extreme cases of infinitely separated atoms and the united atom, and although attention will be primarily directed to the united-atom model, it will be necessary in Chapter 6 to assess the merits of both models as applied particularly to diatomic hydrides.

The mathematical realization of the united atom point of view arises because the wave function for the molecule may be expanded in terms of the functions for the equivalent 'united atom', in the following way. Introducing 'central' potentials $\phi_i = \phi(r_i)$ which are functions of distances from a fixed centre, the molecular Hamiltonian (5.2.2) may be re-written in two

ways, differing in the location of electron repulsion terms (Chen, 1955):

$$H = H^0 + H' = H^{00} + H'' \quad (5.3.1)$$

$$H^0 = \sum_i \left(-\frac{1}{2} \nabla_i^2 + \phi_i \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (5.3.2)$$

$$H' = \sum_i \left(-\phi_i - \sum_{\alpha} \frac{z_{\alpha}}{r_{i\alpha}} \right) \quad (5.3.3)$$

$$H^{00} = H^0 - \sum_{i < j} \frac{1}{r_{ij}} \quad (5.3.4)$$

$$H'' = H' + \sum_{i < j} \frac{1}{r_{ij}} \quad (5.3.5)$$

The solutions of the zero order equations

$$H^0 \psi^0 = E^0 \psi^0, \quad (5.3.6)$$

$$H^{00} \psi^{00} = E^{00} \psi^{00}. \quad (5.3.7)$$

must form a complete set, and the molecular wave function may be expanded in terms of either. The distinct advantage of this approach is that the only integrals that occur are one-centre integrals and it is thus possible to sidestep the mathematical difficulties in computing polycentric integrals as obtained in the more conventional methods.

The most convenient choice of the ϕ_i 's are usually Coulomb or Hooke's law potentials (Chen, 1955) or even $\frac{A}{r_i^2}$, where A is a constant.

The choice of the solutions expressed in terms of the ψ^{00} 's using Coulomb potentials is most suitable for analytical calculations (see Part IV of this thesis), since exact eigenfunctions of H^{00} are known and were discussed in Part I. On the other-hand the choice of the complete set of the ψ^0 's corresponds most closely to the united atom picture, since the ψ^0 's are in fact the eigenfunctions of the united atom. Again Chen, 1955 remarks that this latter choice is highly suitable for the incorporation of the accurate experimental data that exists for atoms (see for example Moore, 1949) and also enables the use of the highly adequate wave functions, for example, Hartree-Fock, Duncanson-Coulson, 1944, as approximations to the ψ^0 's.

The main problem, however, no matter which complete set of functions is used, is to diagonalize the molecular Hamiltonian. Now although the matrix elements of H contain only one-centre integrals, these are in general tedious but are ideally suited for modern high speed electronic computers.

Löwdin, 1957, has described the choice between

the conventional molecular methods using orbitals associated with different nuclei and the united atom model is essentially a choice between the solution of a secular equation of lower order with complicated matrix elements and a secular equation of very high order having simple matrix elements.

The united atom method may be generalized mathematically to an expansion of the molecular wave function with respect to any complete set of functions associated with a single centre in space. If this basic set is discrete, no problem occurs of including the continuum (Löwdin, 1957).

By its very nature, however, the united atom approach cannot be expected to yield direct information concerning the electric field near a nucleus, or of bond properties of molecules, for example, the chemical bond, since these involve mainly the differences between the molecule and its constituent separated atoms. The chief merits of this method is perhaps in molecular spectroscopy, in which this idea has enabled qualitative discussion of electronic energy levels and spectra, and also in quantitative calculation of small molecules with a small extension in space particularly diatomic hydrides. This latter point will be verified in Chapter 6.

3.4 Some Applications of United Atom Theory

It had been believed, hitherto, that the united atom treatment of molecules offers fairly poor approximations for quantitative calculation of molecular energies. During the last eight or nine years, however, there have been attempts to compute the electronic energy levels of molecules and some of their associated constants using the united atom model with a reasonable amount of success.

Matsen (1953) stimulated interests in quantitative calculations using united atom theory by treating H_2^+ from a united atom point of view.

Briefly, the procedure used consisted of writing the Hamiltonian for the hydrogen molecular ion (neglecting nuclear repulsion) in the form

$$-\frac{1}{2} \nabla^2 - \frac{z}{r} + \left(\frac{z}{r} - \frac{1}{r_a} - \frac{1}{r_b} \right) \equiv H_0 + H_1 \quad (5.4.1)$$

r being the distance in Bohrs between the electron and the mid-point between atoms a and b . H_0 may be regarded as the unperturbed Hamiltonian and H_1 as the perturbation (c.f. eqns. (5.3.4) and (5.3.5)). As already discussed in section three of this chapter, the zero order wave functions are then hydrogenic of charge z . Assuming

that non-degenerate perturbation may be applied, the molecular energy to the first order is expressed as

$$\frac{z^2}{2n^2} - 2 \int \frac{V^2 n \ell m}{r_a} dT \quad (5.4.2)$$

The integral (5.4.2) may be evaluated in closed form. Using this result, the $1s\sigma$, $2p\sigma$, $2p\pi$, $3d\delta$ states were calculated for various values of internuclear distance, improved results for the energy being obtained if (5.4.2) is minimized with respect to z (see chapter 6).

Another interesting application of united atom theory was the investigation by Bingel, 1958 and 1961 of the behaviour of the potential energy of both diatomic and polyatomic molecules at small internuclear distances. This investigation showed that the potential energy function V of all states of diatomic and linear polyatomic molecules may be expanded in powers of the distances R_α of the nuclei from the united atom in the form

$$V = \sum_{\alpha > \beta} \frac{z_\alpha z_\beta}{r_{\alpha\beta}} + W_u + \sum_{\alpha} (E_{2,\alpha} R_\alpha^2 + E_{3,\alpha} R_\alpha^3 + \dots) \quad (5.4.3)$$

where W_u is the energy of a particular state u of the united atom. Furthermore it was shown that the quadratic terms $E_{2,\alpha}$ can be explicitly given in terms

of the electronic charge density of the united atom and is independent of the position of the united atom on the molecular axis (Bingel, 1961). If, however, the position of the united atom is chosen as the centre of charge the terms $E_{j,\alpha}$ may be also explicitly determined in terms of the united atom electronic charge density. More generally, if the united atom is fixed as the centre of charge Bingel showed that the expansion (5.4.3) is valid for all molecules together with the expressions for $E_{2,\alpha}$ and $E_{3,\alpha}$. As an added point of interest this analysis shows that the linear term in the expansion of V is zero in accordance with the predictions of Buckingham, 1958.

A slightly different approach to united atom theory was adopted by Bernal (1953) in an attempt to calculate the energy and bond lengths of methane and the ammonium ion NH_4^+ . In this treatment, by expanding the potential V of an electron due to the four protons (the p and d harmonics being zero in the equilibrium position), this potential assumes a spherically symmetric form. This approximation corresponds to the assumption that the protons are smeared over a sphere of radius R_0 , the C-H

or N-H bond length of the molecule and molecular ion respectively. To this approximation for V , the Hamiltonian is formally similar to that for a ten-electron atom, the lowest energy configuration then being the $(1s)^2 (2s)^2 (2p)^6$ ^1S state corresponding to the Neon closed shell. The ground state energies and C-H and N-H bond lengths of methane and NH_4^+ respectively were calculated variationally using scaled analytical antisymmetrized wave functions, the bond length being that value R_0 which minimizes the energy. The results are shown in table (5.4). In particular the calculation of the N-H bond length was an important feature of the results since at that time no experimental value was available.

Using the same united atom approach the energy of methane was calculated by Mills, 1958 using Hartree-Fock wave functions (assuming the C-H bond length to be 2 bohrs) and the results were further improved by including terms of symmetry f in the expansion of V (by using a perturbation technique). These are given in table 5.4.

A similar calculation on the methane molecule was performed by Saturno and Parr, 1960. Again assuming that the protons of the methane molecule are not localized but are smeared over the surface of a sphere of radius R_0 , this spherical model or 'atomic puff' may be described by the neon-like single determinantal wave function. Although this 'atomic puff' has the symmetry of the united atom it was shown that it is energetically more similar to the actual molecule than to the united atom itself. It was further pointed out that the considerable qualitative successes of 'united atom treatments of molecular structure may be due to this fact. Using a variational method the energy of the methane molecule was calculated using this 'atomic puff wave function' and also using a five term wave function similarly centred on the carbon nucleus but having the tetrahedral symmetry of the molecule. The results are again given in table 5.4. For other applications of united atom theory see for example, Chen, 1955 and 1958, Huzinager, 1955; and Hoyland and Parr, 1963 in which one-centre wave functions are used to calculate the diamagnetic

susceptibility and proton shielding constants for the hydrogen molecule; and also the more recent paper by Hank, Parr, and Hamerka 1963.

Table 5.4

Energies and Bond lengths of CH_4 and NH_4^+ in H_R units

Molecule	Calculated energy	Energy (Exp)	R_o	R_o (Exp)
CH_4	-39.33 (a)		1.975(a)	2.0
	-39.38 without f terms			
	{ (b) -40.51			
	-40.06 with f terms			
	-39.50 spherical model			
	{ (c)			
	-39.80 five term result			
NH_4^+	-55.684 (a)		1.836(a)	1.95

(a) Bernal, 1960

(b) Mills, 1958

(c) Saturno and Parr, 1960.

5.5 The Platt electrostatic model of diatomic hydrides

Platt, 1950 succeeded in calculating the inter-nuclear equilibrium distances of diatomic hydrides M-H using a simple united-atom type model. Considering the simplicity of the model used, the results obtained were in remarkably good agreement with experiment. These calculations were based on two hypotheses first, the internuclear equilibrium distance d is near $r_{1.0}$, the radius in the neutral united atom (M+1) at which the effective charge is unity i.e. $r_{1.0}$ is the radius beyond which lie a total of 1.0 electrons. Secondly, the force constant K is approximately given by

$$K = 4\pi\rho_{1.0} \quad (5.5.1)$$

where $\rho_{1.0}$ is the electronic charge density, assumed spherically symmetrical, in the united atom at radius $r_{1.0}$.

Platt justified these hypotheses by an extremely crude application of perturbation theory in the following way. The total electron-density is assumed to be given by the density of the united atom and is held fixed while one proton is removed from the united atom nucleus, analogous to a small perturbation effect. If the proton

is placed inside $r_{1.0}$, it will be attracted by the excess negative charge; outside $r_{1.0}$, however, it will be repelled. Thus to a first approximation, $r_{1.0}$ may be regarded as the equilibrium nuclear distance.

If, further, the proton is displaced a distance dx outward from its equilibrium position, it will be subjected to the attraction of the added shell of charge $4\pi r^2 \rho_{1.0} dx$. The additional attractive force dF on the proton is therefore given by

$$dF = -4\pi r^2 \rho_{1.0} \frac{dx}{r^2}, \quad (5.5.2)$$

so that

$$K = -\frac{dF}{dx} = 4\pi \rho_{1.0} \quad (5.5.3)$$

Since, however, the expression for K depends on the value given to d , Platt computed values of the force constant at the observed values of d and not at $r_{1.0}$ on the grounds that the error in the estimate of the equilibrium internuclear distance would not affect the second hypothesis namely equation (5.5.3) so that the use of the experimental value for d would provide a more valid test of (5.5.3) alone.

The computations were carried out using three different types of wave functions to estimate the electron densities namely, those due to Shull (see Platt, 1950), Hartree orbitals, and where these were not available Slater orbitals. The results were in excellent agreement with experiment, the Shull and Hartree orbitals giving the best fit with the observed values of d and K . Even the Slater orbitals, however, revealed the expected discontinuities in the values of d and K . On the whole, the calculations appeared to predict the force constant more successfully than the equilibrium internuclear distance. Some of the results of Platt's calculations are given in table 6.4 in the next chapter.

5.6 Clinton's derivation and discussion of the Platt model

The simplifying assumptions made by Platt have been discussed by Clinton, 1960, and he points out that since they involve a rigid electronic cloud the quantum mechanical virial theorem is not satisfied at the equilibrium internuclear distance. To show this,

Clinton derives first Platts two results by a slightly different method paying due regard to all the assumptions involved, which, for clarity and conciseness, may be summarized as follows.

- (a) The total electron density is spherically symmetrical about the atom M of nuclear charge z .
- (b) The total electron density is independent of R , the internuclear distance.
- (c) The total electron density is given by the density of the united atom of charge $z+1$.

From assumption (a) the force on the proton in the hydride is given by $W'(R)$ where $W(R)$ is the Born Oppenheimer molecular energy at internuclear distance R , and where

$$W'(R) = -z/R^2 + Q(R)/R^2, \quad (5.6.1)$$

$Q(R)$ being the total electronic charge in a sphere about M of radius R . The equilibrium internuclear distance R_0 is determined from

$$W'(R_0) = 0 \quad (5.6.2)$$

Hence,

$$z = Q(R_0) \quad (6.6.3)$$

The force constant K is therefore given by

$$K = W''(R_0) = -2z/R_0^3 - 2Q(R_0)/R_0^3 + Q'(R_0)/R_0^2 \quad (5.6.4)$$

Using equation (5.6.3) K is therefore given by

$$K = Q'(R_0)/R_0^2 \quad (5.6.5)$$

Now invoking assumptions (b) and (c)

$$K = 4\pi\rho_{ua} \quad (5.6.6)$$

where ρ_{ua} is the united atom electronic density evaluated at $r = R_0$.

Equations (5.6.3) and (5.6.6) thus establish Platt's results. However, this result for the force constant is not in accordance with the virial theorem, which, for a diatomic molecule is expressed by the equation (see appendix)

$$R \frac{\partial W}{\partial R} + 2W = V \quad (5.6.7)$$

where the nucleus M is chosen as origin of coordinates.

Also if ϕ_E is the electronic molecular wave function (assuming the Born-Oppenheimer approximation) and V_E , the total potential energy operator of the system, then V is given by

$$V = \int \phi_E^* V_E \phi_E dT \quad (5.6.8)$$

where the integration is over all electronic co-ordinates.

Clinton shows that assumption (b) violates the virial

theorem in the following way.. Differentiation of (5.6.7) yields

$$\begin{aligned}
 R W''(R) + 3W'(R) &= \frac{\partial V}{\partial R} \\
 &= \frac{\partial}{\partial R} \int \phi_{\epsilon}^* V_{\epsilon} \phi_{\epsilon} d\tau \\
 &= \frac{\partial}{\partial R} \int |\phi_{\epsilon}|^2 V_{\epsilon} d\tau \\
 &= \int |\phi_{\epsilon}|^2 \frac{\partial V_{\epsilon}}{\partial R} d\tau
 \end{aligned} \tag{5.6.9}$$

since $|\phi_{\epsilon}|^2$ is independent of R from assumption (b).

Now, from the Hellmann-Feynmann Theorem (see, for example, Feynmann, 1939)

$$W'(R) = \int |\phi_{\epsilon}|^2 \frac{\partial V_{\epsilon}}{\partial R} d\tau \tag{5.6.10}$$

Hence substituting $W'(R)$ as expressed in (5.6.10) into equation (5.6.9)

$$R W''(R) + \frac{2}{R} W'(R) = 0 \tag{5.6.11}$$

Therefore since $W'(R_0) = 0$ thus implies that

$$K = W''(R_0) = 0 \tag{5.6.12}$$

It is therefore apparent that the assumption of a static electronic charge distribution implies that the force constant vanishes at the equilibrium internuclear distance.

To overcome this difficulty and to explain the success of Platt's results Clinton introduced a correction electron density $\Delta(\underline{r}, R)$ where $\underline{r}$ is measured from the

nucleus M. The exact electron density is therefore

$$\rho(\underline{r}, R) = \rho_{ua}(\underline{r}) + \Delta(\underline{r}, R) \quad (5.6.13)$$

The integral of Δ over all space must, by definition, vanish. Also the dependence of Δ on R ensures a non vanishing force constant. With the assumption that $\rho_{ua}(\underline{r})$ is derived from a non-degenerate state, the force on the proton is then given by

$$W'(R) = [Q(R) - z]/R^2 + F(R) \quad (5.6.14)$$

where $Q(R)$ is defined as before and $F(R)$ is the extra contribution to the force on the proton due to the correction density. The equilibrium condition

$$W'(R_0) = 0 \quad (5.6.15)$$

now gives

$$[Q(R_0) - z]/R_0^2 + F(R_0) = 0 \quad (5.6.16)$$

and the force constant becomes

$$Q'(R_0)/R_0^2 + F'(R_0) + 2F(R_0)/R_0 \quad (5.6.17)$$

using equation (5.6.16).

From (5.6.6), the first term in (5.6.17) is $4\pi\rho_{ua}$, therefore

$$K = 4\pi\rho_{ua} + F'(R_0) + \frac{2}{R_0} F(R_0) \quad (5.6.18)$$

Since the first term in (5.6.18) is the Platt formula, Clinton argued that the last two terms must cancel in

some approximation. Thus if $F(R)$ were of the form λ/R^2 , where λ is a constant

$$\frac{dF}{dR} + \frac{2}{R}F = 0, \quad (5.6.19)$$

would be satisfied for all non-zero values of R . Thus Platt's assumptions are justified if the correction density could be assumed to act on the proton as if it were a point charge. It must be noted, however, that all that is required to explain the accuracy of Platt's formula is that (5.6.19) be satisfied near R_0 , or more specifically at R_0 . $F(R)$ could therefore be any one of many possible functions, for example if F were $\left[\frac{e^{-(R-R_0)}}{R_0 R^2} - \frac{R_0}{R^3} \right]$, the requirement would be satisfied. In many ways a function of this kind is to be preferred, since one would expect the correction density to appear in part, as a dipole and in part as a point charge relative to the proton rather than as a point charge only.

CHAPTER VI

SCALING OF THE PLATT ELECTROSTATIC

MODEL OF DIATOMIC HYDRIDES

6.1 Introduction

Platt's united atom model of diatomic hydrides, as discussed in Chapter V of this thesis, is sufficiently simple to be calculated easily and yet retains enough of the real problem to illustrate its principal features. This is essentially an electrostatic model since it emphasizes the role of the electrostatic forces in determining how far the proton penetrates into the electronic cloud.

In this chapter a modification of the Platt model is proposed which overcomes Clinton's objection of virial violation and improves on Platt's results, especially for the internuclear distances, without becoming any more difficult to understand. The essential change is the introduction of a scale factor into the wave function. The use of the best scale factor for each internuclear distance then ensures that the virial theorem is satisfied automatically. The formulae for the equilibrium internuclear distance and the force constant obtained in this theory are very similar to those of Platt and not very much more complicated to apply.

6.2 The scaled atomic model

In this model, as in Platt's model, the total electron density is taken from atomic calculations. Either the united atom, which corresponds to a nuclear charge, $z + 1$, and zero internuclear distance, or the separated ion, which corresponds to a charge, z , and the total removal of the proton, could be used to provide the electron density. This electron density will be assumed to be spherically symmetrical and its only modification will be a constant scale factor, η , for each internuclear distance.

The Hamiltonian, which governs the electronic structure of a diatomic hydride, has the form, in atomic units

$$H = T_{op} + V_{op} + z/R \quad (6.2.1)$$

where R is the internuclear distance, T_{op} is the usual kinetic energy operator of the N electrons and V_{op} the usual electrostatic potential including the attractions to the nucleus and the proton and the repulsions between the electrons. The approximate atomic wave function is

$$\psi(r_1, \dots, r_N) \quad (6.2.2)$$

and the scaled trial wave function for the hydride is

$$\psi_\eta = \eta^{3N/2} \psi(r_1, \dots, r_N) \quad (6.2.3)$$

The expectation value $T(\eta)$ of T_{op} with respect to this wave-function follows from the fact that T_{op} is homogeneous and of degree -2

$$T(\eta) = \eta^2 T(1) \quad (6.2.4)$$

and this has no explicit dependence on R . On the other hand, the expectation value of V_{op} , which is homogeneous of degree -1, is

$$V(\eta, R) = \eta V(1, \rho) \quad (6.2.5)$$

where $\rho = \eta R$, and depends on R explicitly and through η . The mean value of H becomes, therefore,

$$\begin{aligned} E(\eta, R) &= T(\eta) + V(\eta, R) + z/R \\ &= \eta^2 T(1) + \eta V(1, \rho) + z/R \end{aligned} \quad (6.2.6)$$

The best choice of η is determined by minimizing $E(\eta, R)$ for each value of R and this gives

$$\frac{\partial E}{\partial \eta} = 2\eta T(1) + V(1, \rho) + \rho V_\rho(1, \rho) = 0 \quad (6.2.7)$$

where $V_\rho = \frac{\partial}{\partial \rho} V(1, \rho)$. From this point it will be assumed that η is determined by this equation. It has been shown by Löwdin, 1959a, (see also Appendix) that this choice of η guarantees that the molecular virial relation is satisfied i.e.

$$2T(\eta) + V(\eta, R) + z/R + R \frac{dE}{dR} = 0 \quad (6.2.8)$$

The electronic kinetic energy $T(1)$ is the same as that of the united atom since the same number of electrons and the same wave function is involved. The electronic potential energy differs because of the attraction to the proton and the reduced attraction to the central nucleus so that

$$V(1, \rho) = U - \int \chi(r)/r' d\tau + \int \chi(r)/r d\tau, \quad (6.2.9)$$

where U is the united atom potential energy, $\chi(r)$ the spherically symmetric electron density and r' the distance between electron and proton. Now, by expanding $1/r'$ in terms of spherical harmonics and using the spherical symmetry of $\chi(r)$, the second term in (2.09) becomes

$$\int \chi(r)/r' d\tau = \frac{4\pi}{\rho} \int_0^\rho \chi(r) r^2 dr + 4\pi \int_\rho^\infty \chi(r) r dr \quad (6.2.10)$$

Thus the partial derivative of the potential reduces to

$$V_\rho = \frac{4\pi}{\rho^2} \int_0^\rho \chi(r) r^2 dr \quad (6.2.11)$$

and its second derivative is

$$V_{\rho\rho} = -\frac{8\pi}{\rho^3} \int_0^\rho \chi(r) r^2 dr + 4\pi \chi(\rho). \quad (6.2.12)$$

6.3 Equilibrium distances and force constants

The equilibrium internuclear distance R_0 is determined by the minimum energy i.e.

$$\left(\frac{dE}{dR}\right)_{R_0} = \left(\frac{\partial E}{\partial R} + \frac{\partial E}{\partial \eta} \frac{d\eta}{dR}\right)_{R_0} = 0 \quad (6.3.1)$$

Since η is determined from (6.2.7) this condition simplifies to

$$\left(\frac{dE}{dR}\right)_{R_0} = \left(\frac{\partial E}{\partial R}\right)_{R_0} = (\eta^2 V_\rho - z/R^2)_{R_0} = 0 \quad (6.3.2)$$

It is convenient now to put

$$\eta_0 = \eta(R_0) ; \quad \rho_0 = R_0 \eta_0 \quad (6.3.3)$$

The value of R_0 is therefore fixed by

$$V_{\rho_0} = z/\rho_0^2 \quad (6.3.4)$$

or, using (6.2.11),

$$4\pi \int_0^{\rho_0} \chi(r) r^2 dr = z \quad (6.3.5)$$

This equation is to be compared with the equilibrium condition obtained by Platt i.e.,

$$4\pi \int_0^{R_p} \chi(r) r^2 dr = z \quad (6.3.6)$$

It is clear that the R_p obtained by Platt can be identified as the ρ_0 of this theory and, once η_0 is known, R_0 can be deduced.

The force constant k of the molecule is obtained by

a second differentiation and

$$\begin{aligned}
 k &= \left(\frac{d^2 E}{dR^2} \right)_{R_0} = \left[\frac{d}{dR} (\eta^2 V_p - z/R^2) \right]_{R_0} \\
 &= \left[\frac{\partial}{\partial R} (\eta^2 V_p - z/R^2) + \frac{\partial}{\partial \eta} (\eta^2 V_p - z/R^2) \frac{d\eta}{dR} \right]_{R_0} \quad (6.3.7) \\
 &= 4\pi \gamma(\rho_0) \eta_0^4 (\eta_0 + 4\pi \gamma(\rho_0) \rho_0^2 / 2T(1))^{-1}
 \end{aligned}$$

If the original atomic wave function satisfies the atomic virial theorem, this can be expressed as

$$k = 4\pi \gamma_0 \eta_0^4 (\eta_0 - 4\pi \rho_0^2 \gamma_0 / U)^{-1} \quad (6.3.8)$$

and, from (6.2.7) the value of the scale factor is

$$\eta_0 = 1 - \frac{4\pi}{U} \int_0^{\rho_0} \gamma(r) r \, dr \quad (6.3.9)$$

This is a more elaborate result than that used by

Platt viz.

$$k_p = 4\pi \gamma(R_p) \quad (6.3.10)$$

but the two agree in the limit as $\eta_0 \rightarrow 1$. In addition to the quantities ρ_0 and γ_0 , which are needed in Platt's treatment, the quantities U and the integral in (6.3.9) have to be calculated.

If, instead of the united atom electron density, the separated ion electron density $\bar{\gamma}(r)$ is available, these formulae have to be amended. The potential becomes

$$V(1, \rho) = V - \frac{4\pi}{\rho} \int_0^{\rho} \bar{\gamma}(r) r^2 \, dr - 4\pi \int_{\rho}^{\infty} \bar{\gamma}(r) r \, dr \quad (6.3.11)$$

where V is the potential energy of the free negative ion and $\bar{\gamma}$ is still spherically symmetrical. The

equilibrium condition becomes

$$4\pi \int_0^{\rho_0} \bar{\gamma}(r) r^2 dr = z \quad (6.3.12)$$

and the force constant is

$$k = 4\pi \bar{\gamma}(\rho_0) \eta_0^4 (\eta_0 - 4\pi \rho_0^2 \bar{\gamma}(\rho_0)/7)^{-1} \quad (6.3.13)$$

where the scale factor is now

$$\eta_0 = 1 - \frac{4\pi}{V} \int_0^{\infty} \bar{\gamma}(r) r dr \quad (6.3.14)$$

Again these formulae reduce to Platt's when $\eta_0 \rightarrow 1$.

Now, as the nuclear charge is increased, the potential V increases rapidly whereas the integral in (6.3.14) is always bounded. Thus the separated ion treatment will be the same as Platt's for atoms of large z .

It has been pointed out by Longuet-Higgins and Brown, 1955, and also Bratoz et al., 1960, that Platt's formulae for R_p and k_p can be deduced from the Hellman-Feynmann theorem and this helps to explain why they can be derived using classical electrostatics. The formulae for R_0 and k used here can be deduced in the same way using the scaled electron density but the scale factor itself cannot be found in this way and requires an appeal to the minimum energy principle.

6.4 Results

As a test of the significance of the scale-factor corrections the results obtained for a number of molecules with a small number of electrons are shown in table 4.1. The wave functions used were all of the united atom type and were, for H_2 the simple He function

$$\exp - \frac{27}{16} (r_1 + r_2) ,$$

for LiH the Duncanson - Coulson function for Be (Duncanson and Coulson, 1944) and for HF the Ne function of Sachs, 1961. Since these are not the wave functions used by Platt the table also includes ρ and $4\pi\gamma_0$

Table 4.1 Equilibrium internuclear distances
($\overset{\circ}{A}$) and force constants (10^5 dynes/cm)

	η_0	ρ	R_0	R_p	R_{exp}	$4\pi\gamma_0$	k	k_p	k_{exp}
H_2	0.557	0.42	0.75	0.43	0.74	8.57	4.68	5.4	5.71
Li H	0.861	1.30	1.51	1.39	1.60	1.92	1.20	1.02	1.03
HF	0.88	0.80	0.91	0.87	0.92	14.37	9.70	7.82	9.67

which are the results obtained when Platt's formulae are applied to these wave functions. The table shows that the scaling produces a significant improvement in the equilibrium internuclear distances and especially so for

H_2 . The improvement in the force constants is not so apparent, except for HF, but it has to be remembered that k_{eff} is obtained using the experimental R_{exp} . When the calculated equilibrium internuclear distance R_p is used the improvement in the force constant becomes obvious since this is $4\pi \chi_0$ and is in much poorer agreement with experiment than k .

This sample of the results obtained by introducing a scale factor into Platt's model of the diatomic hydrides is sufficient to show that genuine improvements can be obtained in this way. The improvement is not sufficient, however, to enable more sensitive quantities, such as the dissociation energies, to be predicted.

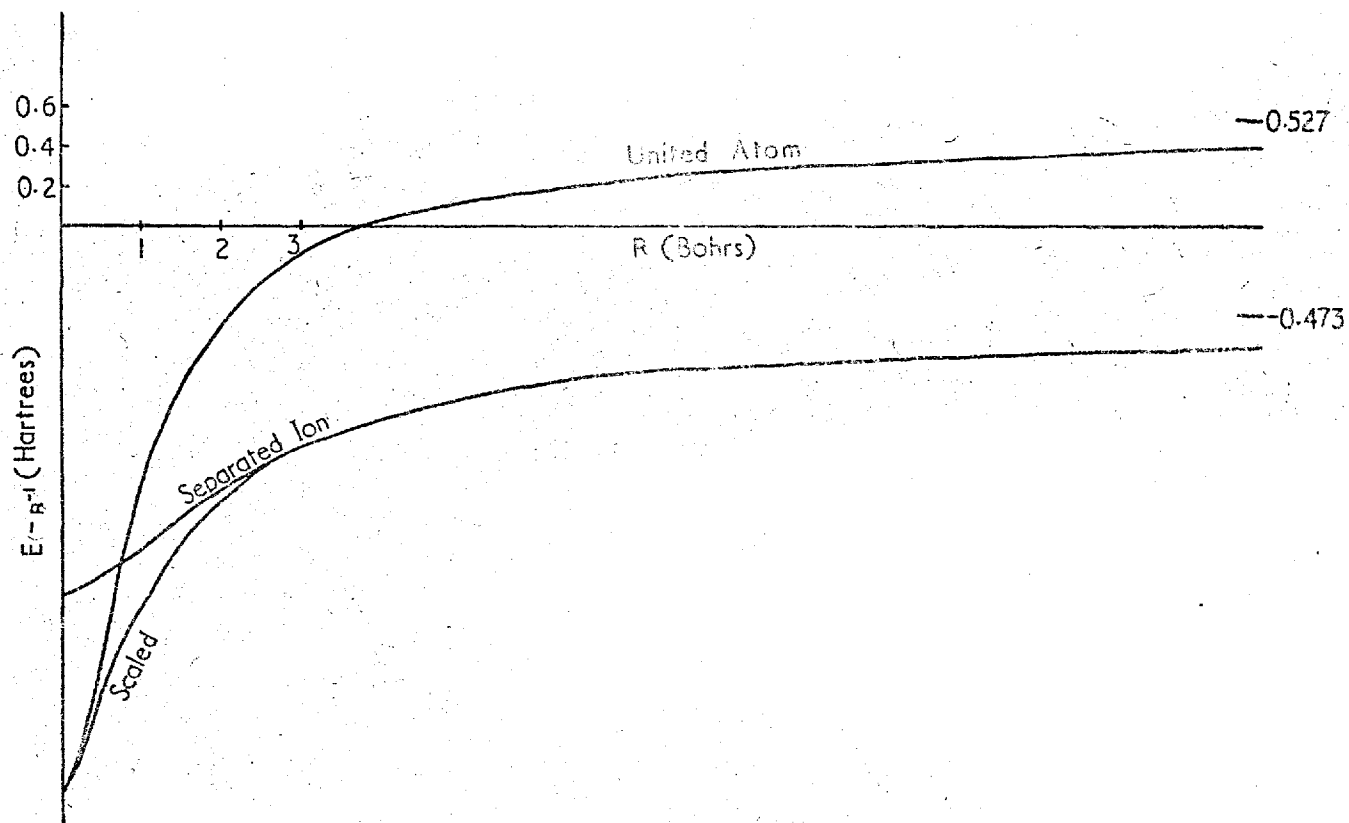
6.5 United atom or separated ion?

In this work, as in Platt's, the initial atomic wave function may be that of the united atom corresponding to $R = 0$ or that of the separated ion which has $R \rightarrow \infty$. Since, for a neutral molecule, the latter is a negative ion and few negative ion wave functions are available the former is much easier to use. From an intuitive point of view, however, it should be a smaller perturbation to bring in a proton from a long distance to the outer

atomic shells than to bring it out through the inner shells. To gain some insight into this problem the example of H_2 has been treated in more detail.

In figure 1, the total electronic energy, $E-R^{-1}$, of H_2 is shown as a function of internuclear distance (see also part IV of this thesis). The energy curves are for the united atom wave function without further scaling, for the separated ion wave function without further scaling and for the scaled function above which has only one parameter and so is both united atom and separated ion in form. As might be expected, the third curve agrees with the united atom one close to $R = 0$ but then diverges considerably. The separated ion curve is very much closer except for very small R . Thus Platt's results for H_2 would be improved by using the separated ion. On the other hand the distinction does not arise when the function is scaled properly though this is not necessarily so for more elaborate atomic functions. The superiority of the separated ion model in the neighbourhood of the equilibrium internuclear distance is further shown by the fact that it gives a force constant of 2.91×10^5 dyne/cm as compared

with the value of 41.25×10^5 dyne/cm given by the united atom model. In part IV comment will be made on the facts that the wave function has incorrect symmetry properties and that the energy, as R increases, is not for the lowest state.



Electronic energy for H_2 ground state.
Figure 1.

PART IV

ISOELECTRONIC SEQUENCES OF

HYDRIDE MOLECULES

CHAPTER 7

THE PERTURBATION EXPANSION - AND EQUILIBRIUM

DISTANCE AND FORCE CONSTANT

7.1 Introduction

The success of the idea of an isoelectronic sequence in the study of atomic structure as discussed in Chapter I has indeed been considerable. It would therefore be highly desirable if there existed a similar concept in the study of molecular spectra. One very good reason which suggests that this in fact might be possible is the success of molecular calculations particularly those on diatomic hydrides which have been based largely on atomic data using the united atom model as discussed in Part III.

The principle purpose of Part IV of this thesis is to show how this idea of an isoelectronic sequence can be extended to diatomic hydrides in which the nuclear charge of the second nucleus is varied freely. By another reformulation the theory is put into a very similar form to the atomic theory and many of the theoretical advantages of this theory are retained. The practical utility of the theory is very limited, however, by the fact that in each sequence there are only a few molecules which are stable with respect to dissociation.

7.2 Perturbation expansion for non-degenerate wave-functions.

There are several different types of isoelectronic sequence of molecules and each will have its own form of theory. In this work the sequences are of diatomic hydrides partly because the nuclear charge of the other nucleus dominates the potential and makes those most like the atomic sequences and partly because the zero order perturbation equations can be solved exactly.

The electronic structure of a diatomic hydride is governed by the Hamiltonian

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i z/r_i - \sum_i 1/r_{iH} + \sum_{i<j} 1/r_{ij}, \quad (7.2.1)$$

where z is the nuclear charge and r_i and r_{iH} the distances between the i th electron and the nucleus and the proton respectively. If, as in section 1.4, a screening constant α is introduced the Hamiltonian will be written as

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i (z-\alpha)/r_i - \alpha \sum_i 1/r_i - \sum_i 1/r_{iH} + \sum_{i<j} 1/r_{ij} \quad (7.2.2)$$

where α the molecular screening parameter will be

discussed later. The units implied in this Hamiltonian are the usual atomic units. To obtain a more useful form of the Hamiltonian the unit of charge is changed to $e\sqrt{(z - \alpha)}$ without changing the units of mass or of action. This results in the usual changes in the length i.e. $(z - \alpha)$ Bohrs and in the energy i.e. $(z - \alpha)^2$ Hartrees. In these units the Hamiltonian becomes

$$H = H_0 + (z - \alpha)^{-1} H_1, \quad (7.2.3)$$

with

$$H_0 = \sum_i \left(-\frac{1}{2} \nabla_i^2 - 1/r_i \right) \quad (7.2.4)$$

$$H_1 = \sum_{i < j} 1/r_{ij} - \alpha \sum_i 1/r_i - \sum_i 1/r_{iH} \quad (7.2.5)$$

The importance of this step in the argument as in the case of isoelectronic sequences of atoms is that it enables the zero-order wave function to be found exactly since the zero-order Hamiltonian H_0 separates into hydrogen atom Hamiltonians for each electron and the zero-order wave function Ψ_0 will consist of one or more determinants of hydrogen atom orbitals. In this section it will be assumed that the ground state energy is non-degenerate so that Ψ_0 is a single determinant. The perturbation expansion now has the form

$$\underline{\Psi} = \underline{\Psi}_0 + (z-\alpha)^{-1} \underline{\Psi}_1 + \dots \quad (7.2.6)$$

$$W = W_0 + (z-\alpha)^{-1} W_1 + (z-\alpha)^{-2} W_2 + (z-\alpha)^{-3} W_3 + \dots \quad (7.2.7)$$

This use of $(z-\alpha)^{-1}$ as the expansion parameter instead of z^{-1} greatly assists the convergence of the series for an atom, see section 1.5, and is even more important for a molecule. Each term in the expansion of the wave function determines two terms in the expansion of the energy, (Dalgarno and Stewart, 1956), so that, for example, if $\underline{\Psi}_0$ is normalized the first two terms in the energy are

$$W_0 + (z-\alpha)^{-1} W_1 = \int \underline{\Psi}_0^* \{H_0 + (z-\alpha)^{-1} H_1\} \underline{\Psi}_0 d\tau \quad (7.2.8)$$

or, in the original Hartree units

$$(z-\alpha)^2 \int \underline{\Psi}_0^* H \underline{\Psi}_0 d\tau \quad (7.2.9)$$

This is the energy that would have been obtained using a trial wave function in the form of a determinant of hydrogen atom functions each with the scale factor $(z-\alpha)$. This suggests that the value of α should be fixed by minimizing those first two terms for each value of the internuclear distance. The value of α found in this way may not be the best one to ensure the most rapid convergence of the series for the energy but it should be sufficiently good for present purposes (cf table 1.5 in Chapter 1).

When the internuclear distance vanishes the electronic Hamiltonian reduces to that for the united atom. At the other limit when the internuclear distance is very large the proton is effectively removed leaving all the electrons around the other nucleus. The resulting ion, i.e. the separated ion, is isoelectronic with the united atom but has a nuclear charge less by one. Thus if α increases by one as the internuclear distance varies from zero to infinity the coefficients in the energy expansion must be the same at both limits. In particular, the method of choosing α adopted above satisfies this requirement and so will help to keep the variations in the coefficients with internuclear distance small. This emphasis on a smooth curve connecting the two limits leads unfortunately to several complications. Thus, for neutral molecules, the separation into ions at large distances means that the calculated energy does not follow one energy eigenvalue but crosses smoothly over several in order to preserve the ionic nature of the wave function. If the crossings are far from the equilibrium distance and if allowances are made when calculating dissociation energies this

passing from one potential to another may not be a major disadvantage. Another complication is that there are states which are important for certain nuclear charges and for intermediate distances which cannot easily be brought into the theory since they correspond to continuum states at the limits.

The form of the electronic energy in terms of the original Hartree units is now

$$W = (z-\alpha)^2 W_0 + (z-\alpha)W_1 + W_2 + (z-\alpha)^{-1}W_3 \dots \quad (7.2.10)$$

where α , W_0 and W_1 , can be calculated using only the hydrogen atom orbitals. The various W_r are functions of the modified internuclear distance which is

$$\rho = (z - \alpha)R \quad (7.2.11)$$

where R is the actual internuclear distance in Bohrs.

7.3 Perturbation expansion for degenerate wave functions.

For most states of most diatomic hydrides the perturbation method described above needs to be modified before it can be applied. In precisely the same way as degenerate isoelectronic expansions for atoms (see section 1.3), this is due to the degeneracy of the zero-order wave function which arises because of the degeneracy of

the hydrogen atom orbitals. Thus, in general, there will be a number of determinantal wave functions with the same energy and the appropriate linear combination has to be found using degenerate perturbation theory and diagonalizing the matrix of the perturbation. An alternative formulation which leads to the same result is that the energy should be minimized with respect to the coefficients in the linear combination. This shows that the perturbation now effects the wave function to zero order and so leads to an additional lowering of the first order correction to the energy. When the best linear combination of determinants has been substituted for Ψ_0 the discussion and equations in section 7.2 remain valid.

As the number of electrons in the molecule is increased so the number of degenerate wave functions tends to increase though there are several counteracting features. The first of these is the Pauli principle and this is sometimes sufficient, for example in the ground state of the 10 electron sequence, to lead to non-degeneracy. The second is the existence of selection rules due to spin and to the axial symmetry ($C_{\infty h}$) which still apply. The $^3 \Sigma^-$ ground state of the 8 electron

sequence, for example, has no degeneracy except that due to the triplet which can be resolved easily by using S_z .

The calculation of the matrix elements of the energy with respect to those zero-order atomic wave functions is made easier by certain selection rules which apply to the different terms in the energy. Since part of the perturbation is a one-electron operator its matrix elements vanish between wave functions which differ in respect to two or more orbitals. On the other hand the two-electron part has spherical symmetry and so has zero matrix elements between wave functions of different spherical symmetry even though they have the same axial symmetry.

This extension of the theory to include degeneracy means that effects such as the angular correlation effects discussed by Linderberg and Shull, 1960 are now included in the theory.

7.4 The total energy, equilibrium distance and force constant.

The expansion of the total electronic energy for the N electron sequence, whether degeneracy occurs or not, has the form

$$W = (z - \alpha)^2 W_0 + (z - \alpha) W_1 + W_2 + \dots \quad (7.4.1)$$

The first coefficient W_0 is the sum of contributions of $-\frac{1}{2}$ for each 1s electron and of $-\frac{1}{8}$ for each 2s or 2p electron and is independent of ρ . For the non-degenerate case, W_1 is the mean value of the perturbation and so depends on both ρ and α . When there is degeneracy, W_1 is determined by diagonalizing a finite matrix whose elements are the matrix elements of H_1 . Now α appears in H_1 as a multiple of a one-electron spherical potential and the selection rules ensure that α will then enter only the diagonal matrix elements and with the same coefficient. Thus, in either event W_1 has the form

$$W_1 = f(\rho) - C\alpha, \quad (7.4.2)$$

where f depends only on ρ and C is a constant which has the value $-2W_0$.

The total energy, E , of a diatomic hydride when the electronic energy is taken up to the third term is now

$$E = (z - \alpha)^2 W_0 + (z - \alpha)[f - C\alpha] + W_2(\rho) + z/R \quad (7.4.3)$$

Although W_2 will not be calculated here it is desirable to include it in order to be able to estimate its effect empirically. The scale factor α is determined by minimization so that, at constant R ,

$$\frac{dE}{d\alpha} = C\alpha - f - \rho f' - RW_2' = 0 \quad (7.4.4)$$

When W_2 is omitted this equation determines α as a function of ρ and hence of R . The equilibrium internuclear distance R_0 is defined as the value which minimizes the energy so that it satisfies

$$\left(\frac{dE}{dR}\right)_{R_0} = \left(\frac{\partial E}{\partial R} + \frac{dE}{d\alpha} \frac{d\alpha}{dR}\right)_{R_0} = 0 \quad (7.4.5)$$

and, since α satisfies

$$\frac{dE}{d\alpha} = 0, \quad (7.4.6)$$

this condition simplifies to

$$\frac{\partial E}{\partial R} = [(z-\alpha)^2 [f' - z/\rho^2] + (z-\alpha)W_2']_{R_0} = 0 \quad (7.4.7)$$

When W_2' is omitted this equation for R_0 can be written as

$$f'(\rho_0) = z/\rho_0^2 \quad (7.4.8)$$

where

$$z - \alpha(\rho) = \eta, \quad z - \alpha(R_0) = \eta_0, \quad \rho_0 = R_0 \eta_0 \quad (7.4.9)$$

This equation is very similar in form to equation (6.3.4) obtained in Chapter 6, using a scaled form of the Platt model i.e.

$$\frac{\partial V}{\partial \rho_0} = z/\rho_0^2 \quad (7.4.10)$$

where V is the electronic potential energy and this reduces to the more explicit form

$$4\pi \int_0^{\rho_0} \gamma(r) r^2 dr = z \quad (7.4.11)$$

where $\gamma(r)$ is the spherically symmetric electron density due to the zero-order wave function.

The force constant, k , is defined as the second derivative of the total energy at R_0 and, after some manipulation, can be reduced to the formula

$$k = \left(\frac{d^2 E}{dR^2} \right)_{R_0} = \eta_0^4 \{ f''(\rho_0) + 2z/\rho_0^3 + W_2''(\rho_0)/\eta_0 - [W_2'(\rho_0)]^2 / c\eta_0^3 \} / \{ \eta_0 + \rho_0^2 / c [f''(\rho_0) + 2z/\rho_0^3 + W_2''(\rho_0)/\eta_0] \} \quad (7.4.12)$$

When W_2 is omitted this takes the form

$$k = \eta_0^4 \{ f''(\rho_0) + 2z/\rho_0^3 \} / \{ \eta_0 + \rho_0^2 / c [f''(\rho_0) + 2z/\rho_0^3] \} \quad (7.4.13)$$

which is again similar to the corresponding formula given by equation (6.3.8) in Chapter 6.

CHAPTER 8

APPLICATIONS TO THE ONE, TWO AND FOUR ELECTRON SEQUENCES

8.1 Introduction.

In Chapter 8, the perturbation expansions of the previous chapter are applied to the one, two, and four electron sequences i.e. to H_2^+ , H_2 , LiH and their associated ions. The one and two electron sequences furnish examples of the non-degenerate expansion while the four electron sequence illustrates the theory when there is degeneracy. The zero and first order expansion coefficients are computed for these sequences and their equilibrium distances and force constants investigated. It is also shown that higher order terms are needed to explain the basic properties of the molecules.

8.2 Application to the one and two electron sequences.

The relations between this perturbation theory and other theories can be conveniently illustrated using the one electron sequence. Since the electron is in the field of a nucleus of charge z and a proton separated at distance R from it, the electronic Hamiltonian, in atomic units is

$$H = -\frac{1}{2} \nabla^2 - (z - \alpha)/r - (\alpha/r + 1/r_H) . \quad (8.2.1)$$

When the unit of charge is increased to $e\sqrt{(2-\alpha)}$, the Hamiltonian becomes

$$\left(-\frac{1}{2}\nabla^2 - 1/r\right) = (2-\alpha)^{-1}(\alpha/r + 1/r_H) \quad (8.2.2)$$

where the separation of the nuclei is now ρ .

The exact zero order wave function is

$$\psi_0 = \pi^{-1/2} e^{-r} \quad (8.2.3)$$

and the energy expansion has

$$W_0 = -\frac{1}{2} \quad (8.2.4)$$

and

$$\begin{aligned} W_1 &= -\int \psi_0 (\alpha/r + 1/r_H) \psi_0 d\tau \\ &= -\alpha - \rho^{-1}[1-(1+\rho)e^{-2\rho}]. \end{aligned} \quad (8.2.5)$$

By minimizing the first two terms in the energy with respect to α , α is determined as

$$\alpha = -(1+2\rho)e^{-2\rho} \quad (8.2.6)$$

and varies from -1 at $\rho = 0$ to 0 as $\rho \rightarrow \infty$. At both limits the perturbation vanishes and ψ_0 becomes the entire exact solution.

From these first two terms in the energy an approximation to the energy potential can be obtained but it is not satisfactory. The equilibrium distance R_0 , for example is obtained from the equation

$$\frac{d}{dR} (W + z/R)_{R=R_0} = 0 \quad (8.2.7)$$

This reduces for H_2^+ to the equation

$$(1 + 2\rho_0 + 2\rho_0^2) e^{-2\rho_0} = 0 \quad (8.2.8)$$

which cannot be satisfied for any finite value of ρ_0 which means that the potential is purely repulsive.

The third term in the energy series can be included in the treatment in various ways. The perturbation calculation of Dalgarno and Lynn, 1957 gives this term exactly but only for $\alpha = 0$. An alternative procedure would be to use the known energy curve for H_2^+ to fit a suitable form of the third term. The details of this process are discussed later in this Chapter. In principle this could be used to predict the energy curves for other values of z but in practice there are two complications. The first is that the hydrogen molecular ion is the only member of the sequences to have a stable equilibrium internuclear distance. The second is that for $z = 1$ the two nuclei become identical and a wave function of the form assumed is no longer sufficiently accurate to give good results. The identity of the centres leads, in fact, to an unusually large perturbation and so is not properly used in an

extrapolation to other z .

Unfortunately, some of the difficulties of the one-electron sequences are still found in the two-electron sequences although others are eliminated. The Hamiltonian is again modified by a change of scale and rearranged into the form

$$\begin{aligned} & \left(-\frac{1}{2} \nabla_1^2 - 1/r_1 \right) + \left(-\frac{1}{2} \nabla_2^2 - 1/r_2 \right) + \\ & (z-\alpha)^{-1} (1/r_{12} - 1/r_{1H} - 1/r_{2H} - \alpha/r_1 - \alpha/r_2) \end{aligned} \quad (8.2.9)$$

The exact zero order wave function is

$$\psi_0 = \pi^{-1} \exp(-r_1 - r_2) \quad (8.2.10)$$

and the first two energy terms are

$$W_0 = -1 \quad (8.2.11)$$

$$\begin{aligned} W_1 &= \int \psi_0 (1/r_{12} - 1/r_{1H} - 1/r_{2H} - \alpha/r_1 - \alpha/r_2) \psi_0 d\tau \\ &= -2/\rho \{ 1 + (1+\rho)e^{-2\rho} \} + 5/8 - 2\alpha \end{aligned} \quad (8.2.12)$$

If the best value of α is defined as the one which minimizes these two terms in the energy then

$$\alpha = 5/16 - (1+2\rho)e^{-2\rho} \quad (8.2.13)$$

so that α varies from $-11/16$ at $\rho = 0$ to $5/16$ as $\rho \rightarrow \infty$.

The equilibrium internuclear distance is found by differentiating the total energy and, for $z = 1$ and the best value of α , this leads to

$$1 = (2 + 4\rho_0 + 4\rho_0^2)e^{-2\rho_0} \quad (8.2.14)$$

which may be solved to give

$$\rho_0 = 1.336 \quad (8.2.15)$$

This results in a calculated separation of

$$R_0 = 1.42 \text{ Bohrs.} \quad (8.2.16)$$

compared with the experimental value of 1.40 B.

Similarly the force constant is calculated to be 0.301

compared with the experimental 0.371. For $z = 2$,

however, the potential given by the first two terms in purely repulsive.

8.3 Application to the four-electron sequence

The application of the theory when there is degeneracy can be illustrated by reference to the four-electron sequence. The ground state of this sequence has the symmetry ${}^1\Sigma$ and there are four degenerate zero-order wave functions which contribute to it.

These are, in spectroscopic notation,

$$(1S)^2 (2S)^2 \quad {}^1S$$

$$(1S)^2 (2S, 2p_z) \quad {}^1P \quad (L_z = 0 \text{ component})$$

$$(1S)^2 (2p)^2 \quad {}^1S$$

$$(1S)^2 (2p)^2 \quad {}^1D \quad (L_z = 0 \text{ component})$$

These give rise to a 4 x 4 matrix whose eigenvalues determine W_1 . The elements H_{ij} in this matrix are simplified by using the selection rules mentioned above. The integrals involving the electrostatic repulsions are available in Linderberg and Shull 1960 as already discussed in section 2.2. The parameter α appears explicitly only on the diagonal and can be omitted from the diagonalization. The remaining matrix elements are either constants or are functions of ρ . For the four electron sequence these matrix elements are:

$$H_{11} = 1.57100105 - \frac{2}{\rho} [1 - (1 + \rho)e^{-2\rho}] - \frac{2}{\rho} [1 - (1 + \frac{3}{4}\rho + \frac{\rho^2}{4} + \frac{\rho^3}{8})e^{-\rho}] - \frac{5\alpha}{2} \quad (8.3.1)$$

$$H_{22} = 1.68273760 - \frac{2}{\rho} [1 - (1 + \rho)e^{-2\rho}] - \frac{1}{\rho} [2 + \frac{12}{\rho^2} - (\frac{12}{\rho^2} + \frac{12}{\rho} + 8 + \frac{7}{2}\rho + \rho^2 + \frac{\rho^3}{4})e^{-\rho}] - \frac{5\alpha}{2} \quad (8.3.2)$$

$$H_{33} = 1.77884915 - \frac{2}{\rho} [1 - (1 + \rho)e^{-2\rho}] - \frac{2}{\rho} [1 - (1 + \frac{3}{4}\rho + \frac{\rho^2}{4} + \frac{\rho^3}{24})e^{-\rho}] - \frac{5\alpha}{2} \quad (8.3.3)$$

$$H_{44} = 1.74720853 - \frac{2}{\rho} [1 - (1+\rho)e^{-2\rho}] - \frac{5\alpha}{2} \\ - \frac{2}{\rho} \left[1 + \frac{6}{\rho^2} - \left(\frac{6}{\rho^2} + \frac{6}{\rho} + 4 + \frac{7}{4}\rho + \frac{\rho^2}{4} + \frac{\rho^3}{12} \right) e^{-\rho} \right] \quad (8.3.4)$$

$$H_{12} = H_{21} = \frac{3}{\rho^2} \left[1 - \left(1 + \rho + \frac{\rho^2}{2} + \frac{\rho^3}{6} + \frac{\rho^4}{24} \right) e^{-\rho} \right] \quad (8.3.5)$$

$$H_{23} = H_{32} = \frac{\sqrt{3}}{\rho^2} \left[1 - \left(1 + \rho + \frac{\rho^2}{2} + \frac{\rho^3}{6} + \frac{\rho^4}{24} \right) e^{-\rho} \right] \quad (8.3.6)$$

$$H_{13} = H_{31} = 0.050743672 \quad (8.3.7)$$

$$H_{24} = H_{42} = -\frac{\sqrt{6}}{\rho^2} \left[1 - \left(1 + \rho + \frac{\rho^2}{2} + \frac{\rho^3}{6} + \frac{\rho^4}{24} \right) e^{-\rho} \right] \quad (8.3.8)$$

$$H_{34} = H_{43} = \frac{\sqrt{2}}{\rho} \left[+ \frac{12}{\rho^2} - \left(\frac{12}{\rho^2} + \frac{12}{\rho} + 6 + 2\rho + \frac{\rho^2}{2} + \frac{\rho^3}{12} \right) e^{-\rho} \right] \quad (8.3.9)$$

$$H_{14} = H_{41} = 0 \quad (8.3.10)$$

The matrix consisting of the above elements has to be diagonalized and its eigenvalues found for a range of values of ρ in order to determine $f(\rho)$.

The evaluation of the matrix elements for each ρ and the calculation of the eigenvalues have been programmed for the English Electric DEUCE computer. Care is needed in evaluating the matrix elements since, for certain ρ , they involve considerable cancellations between polynomials and exponentials. This is overcome

by arranging the formula so that these exponentials are evaluated as power series and the cancellation carried out analytically. The eigenvalues were calculated for values of ρ at intervals of 0.25 Bohr between $\rho = 0.25$ Bohr and $\rho = 15$ Bohr. The derivatives of f were found by numerical differentiation. The equilibrium value of ρ was found from the equation by inverse interpolation and then the corresponding value of α . The internuclear distance R_0 and the force constant k are readily deduced from equations (7.4.8) and (7.4.13). The results obtained for the ground state and for the first excited state which has the same symmetry as the ground state are shown in Table 1. The experimental results quoted in comparison are taken from Herzberg, 1950. The large discrepancies between

Table 1. Calculated and experimental internuclear distances and force constants.

Molecule	State	$z=\alpha_0$	ρ_0 (Bohrs)	R_0 (Å)	R_{exp} (Å)	$k(10^5)$ dynes/cm	$k_{exp}(10^5)$ dynes/cm
LiH	ground	2.443	5.015	1.086	1.595	4.263	1.026
	excited	2.416	4.596	1.007	2.596	5.791	0.029
BeH ⁺	ground	3.378	8.444	1.323	1.312	0.812	2.633
	excited	3.342	6.442	1.020	1.609	5.541	1.162

calculation and experiment suggest very strongly $W_2(\rho)$ needs to be included in the calculation before significant predictions can be made. This is the next term in the perturbation series and could be calculated by finding the first order correction to the wave function. Instead of doing this its effect will be estimated empirically.

Since $W_2(\rho)$ does not depend explicitly on z its effect can be estimated by equating theory and experiment for one molecule and using the results to predict the effect for another molecule. Since W_2 ought to be a smooth function of ρ in the neighbourhood of the equilibrium it is expanded as a Taylor series about the equilibrium ρ_0 for the first molecule

$$W_2(\rho) = W_2(\rho_0) + (\rho - \rho_0)W_2'(\rho_0) + \frac{1}{2}(\rho - \rho_0)^2 W_2''(\rho_0) \quad (8.3.11)$$

The experimental internuclear distance and force constant for the first molecule are then used to determine $W_2'(\rho_0)$ and $W_2''(\rho_0)$. The value of $W_2(\rho_0)$ could be fixed if the experimental total energy were known accurately enough but it is usually better to leave it undetermined.

For the four-electron sequence the molecule LiH was taken as the known molecule and its data used to predict

corresponding results for BeH^+ . By eliminating W_2 from the equations defining ρ_0 and α_0 it follows that

$$C\alpha_0 = f(\rho_0) + z/\rho_0 \quad (8.3.12)$$

so that the relation between α_0 and ρ_0 is unchanged by the inclusion of W_2 . The value of ρ corresponding to equilibrium is changed, however, because of the extra term. Its new value ρ_0' , may be determined by using the experimental distance, R_{exp} , the relation between α_0 and ρ_0 and the iteration formula

$$(\rho_0')_{n+1} = [z - \alpha((\rho_0')_n)]R_{\text{exp}} \quad (8.3.13)$$

Once the consistent value of ρ_0' has been found the original definition of the equilibrium distance becomes an equation for $W_2'(\rho_0')$. The corresponding value of $W_2''(\rho_0')$ follows from the experimental force constant. For the ground state of LiH the consistent value of ρ_0' is 7.332 and the expansion of W_2 becomes

$$W_2(\rho) = W_2(\rho_0') - (\rho - \rho_0')0.038025 + \frac{1}{2}(\rho - \rho_0')^2 0.015289 \quad (8.3.14)$$

With this form for W_2 the results for BeH^+ were recalculated and are 1.512 Å for R_0 and 2.301×10^5 dynes/cm for k . The former is made worse by the inclusion of W_2

although the latter is considerably improved. A secondary result which follows from this calculation is that E' has no zero for $z > 4.1$ in the ground state and for $z > 4.5$ in the excited state. Thus the theory predicts that the energy curves for CH^{++} and higher members of the sequence are purely repulsive.

While these numerical results are disappointing they are better than might have been expected physically. The LiH molecule is well known to be close to ionic in its binding with the hydrogen negative ion, yet this theory uses a wave function in which the electrons are all centered on the Li. The mixture of determinants ensures, however, that the zero-order wave function does have a substantial dipole moment in the direction of the proton.

8.4 Conclusions

The first quantitative results of this theory of diatomic hydrides are very much less encouraging than for the corresponding theory of atomic isoelectronic sequences. This must be attributed to the fact that the zero-order wave function is a much cruder

approximation in relation to the molecules than to the atoms. The theory will have to be carried to higher order before significant agreement with experiment can be expected.

The significance of this theory is that it is a method of investigating molecular structure using perturbation theory and stressing the possibility of varying the nuclear charge. By using, as a first approximation, a wave function which interpolates between the united atom and the separated ion it also provides some interesting cross-connections between various physical ideas. Its relation to the Platt model is particularly close although its restriction to hydrogenic orbitals instead of self-consistent ones makes the numerical results much less accurate. A modification of the theory to permit more accurate orbitals without complicating the expansion is very desirable.

Although the applications in this part of the thesis have been restricted to diatomic hydrides because these are best known it is trivial to extend the theory to polyatomic molecules which have one heavy atom and a number of hydrogens.

Appendix

1. The quantum mechanical virial theorem for atoms

The Hamiltonian which governs the electronic structure of atoms, has the form, in atomic units

$$H = T_{op} + V_{op} \quad (1.1)$$

where

$$T_{op} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (1.2)$$

$$V_{op} = - \sum_{i=1}^N \frac{z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \quad (1.3)$$

as already defined in Chapter 1. T_{op} is therefore the usual kinetic energy operator of the N electrons and V_{op} the usual electrostatic potential including the attractions to the nucleus. Consider now an approximate wave function

$$\psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \quad (1.4)$$

and a scale factor η . The scaled trial wave function then becomes

$$\psi_\eta = \eta^{3N/2} \psi(\underline{r}_1, \dots, \underline{r}_N) \quad (1.5)$$

The expectation values $T(\eta)$ of T_{op} and similarly $V(\eta)$ of V_{op} with respect to this wave function follows from the fact that T_{op} is homogeneous of degree -2 and V_{op} is homogeneous of degree -1 .

$$T(\eta) = \eta^2 T(1) \quad (1.6)$$

$$V(\eta) = \eta V(1) \quad (1.7)$$

The mean value of H becomes therefore

$$\begin{aligned} E(\eta) &= T(\eta) + V(\eta) \\ &= \eta^2 T(1) + \eta V(1) \end{aligned} \quad (1.8)$$

The best choice of η is determined by minimising $E(\eta)$ and this gives

$$\frac{\partial E}{\partial \eta} = 2\eta T(1) + V(1) = 0 \quad (1.9)$$

giving

$$\eta = -V(1)/2T(1) \quad (1.10)$$

Substitution of the value of η from equation (1.10) into equations (1.6) and (1.7) give

$$T(\eta) = V^2(1)/4T(1) \quad (1.11)$$

$$V(\eta) = -V^2(1)/2T(1) \quad (1.12)$$

and consequently

$$T(\eta) = -\frac{1}{2} V(\eta) \quad (1.13)$$

Equation (1.13) is the atomic virial theorem for approximate wave functions using a scale factor η which satisfies equation (1.9). The virial theorem for an exact wave function follows immediately. If ψ is an exact wave function, then the variation principle given by equation (1.9) must be fulfilled for $\eta = 1$, and

substitution of this value into equation (1.10) gives

$$T(1) = -\frac{1}{2} V(1) \quad (1.14)$$

and hence from equation (1.8)

$$E(1) = \frac{1}{2} V(1) \quad (1.15)$$

2. The quantum mechanical virial theorem for diatomic hydrides.

Assuming the Born-Oppenheimer approximation, the Hamiltonian governing the electronic structure of a diatomic hydride is, as already given by equation (6.2.1)

$$H = T_{op} + V_{op} + z/R \quad (2.1)$$

If an approximate trial wave function, which, in general will depend on the internuclear distance, is scaled with a scale factor

$$\psi(\eta, R) = \eta^{3N/2} \psi(\eta r_1 \dots, \eta r_N; \rho) \quad (2.2)$$

and also

$$T(\eta, R) = \eta^2 T(1, \rho) \quad (2.3)$$

$$V(\eta, R) = \eta V(1, \rho) \quad (2.4)$$

where $\rho = \eta R$ as already discussed in section 6.2 of this thesis, the important difference now being that due to the

explicit dependence of ψ on R , the expectation value of T_{op} depends on R explicitly and not only through η . The mean value $E(\eta, R)$ becomes therefore

$$\begin{aligned} E(\eta, R) &= T(\eta, R) + V(\eta, R) + z/R \\ &= \eta^2 T(1, \rho) + \eta V(1, \rho) + z/R. \end{aligned} \quad (2.5)$$

η is determined by minimising $E(\eta, R)$ for each value of R and this gives

$$\frac{\partial E}{\partial \eta} = 2\eta T(1, \rho) + \eta \rho T_\rho(1, \rho) + \rho V_\rho(1, \rho) + V(1, \rho) = 0 \quad (2.6)$$

Differentiating E with respect to R gives

$$\frac{dE(\eta, R)}{dR} = \frac{\partial E(\eta, R)}{\partial R} + \frac{\partial E(\eta, R)}{\partial \eta} \cdot \frac{\partial \eta}{\partial R} \quad (2.7)$$

If, from this point on, it is assumed that η satisfies equation (2.6) then

$$\begin{aligned} \frac{dE(\eta, R)}{dR} &= \frac{\partial E(\eta, R)}{\partial R} \\ &= \eta^3 T_\rho(1, \rho) + \eta^2 V_\rho(1, \rho) - z/R^2 \end{aligned} \quad (2.8)$$

Multiplying equation (2.6) by η gives

$$2\eta^2 T(1, \rho) + \eta V(1, \rho) + R[\eta^3 T_\rho(1, \rho) + \eta^2 V_\rho(1, \rho)] = 0 \quad (2.9)$$

and using equations (2.3), (2.4) and (2.8) the following result is obtained

$$2T(\eta, R) + V(\eta, R) + z/R + R \frac{dE(\eta, R)}{dR} \quad (2.10)$$

This is the molecular virial theorem for approximate wave functions which holds if they are correctly scaled. It is to be noted that this result holds whether or not the trial wave function is atomic i.e. whether or not it has explicit dependence on the internuclear distance R . If ψ is the exact solution, since the variation principle is then fulfilled for $\eta = 1$, equation (2.10) becomes

$$2T(1,R) + V(1,R) + z/R + R \frac{dE(1,R)}{dR} = 0 \quad (2.11)$$

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