MODEL POTENTIALS AND MOLECULAR RYDBERG SERIES
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By

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy.

McMaster University
August 1973
DEDICATION

To my Parents

"And here are trees and I know their gnarled surface, water and I feel its taste. These scents of grass and stars at night, certain evenings when the heart relaxes--how shall I negate this world whose power and strength I feel? Yet all the knowledge on earth will give me nothing to assure me that this world is mine. You describe it to me and you teach me to classify it. You enumerate its laws and in my thirst for knowledge I admit that they are true. You take apart its mechanism and my hope increases. At the final stage you teach me that this wondrous and multicolored universe can be reduced to the electron. All this is good and I wait for you to continue. But you tell me of an invisible planetary system in which electrons gravitate around a nucleus. You explain this world to me with an image. I realize then that you have been reduced to poetry: I shall never know. Have I the time to become indignant? You have already changed theories...."

Albert Camus
The Myth of Sisyphus
DOCTOR OF PHILOSOPHY (1973) McMASTER UNIVERSITY
(Chemistry) Hamilton, Ontario

TITLE: Model Potentials and Molecular Rydberg Series.

AUTHOR: Frank Richard Greening, B.Sc. (King's College, London)

SUPERVISOR: Professor G.W. King

NUMBER OF PAGES: ix, 162

SCOPE AND CONTENTS:

Model potential calculations have been carried out on the $q \rightarrow n\sigma_g$, $np_u$ and $np_u$ Rydberg series of $CO_2$, $CS_2$ and $CSe_2$. The molecular potential was represented by a superposition of atomic model potentials which were calibrated to atomic data. The Rydberg M.O. was expanded about the molecular mid-point in a linear combination of hydrogen functions and many members of a Rydberg series were obtained in a single calculation on a computer. The results of the calculations were used to check previous assignments of Rydberg series in $CO_2$ and $CS_2$. The previously unreported vacuum u-v spectrum of $CSe_2$ was observed in the region from 1200-2000 Å, and analysed using the model calculations.
ACKNOWLEDGEMENTS

I wish to thank Dr. G.W. King for allowing me complete freedom in my research while still providing the advice and encouragement that was often needed. I wish also to thank Dr. D.P. Santry for considerable assistance with the computational aspects of my research.

I wish to thank my research colleagues, Dr. E.J. Finn and Dr. P. Pichat, for experimental assistance and helpful discussions, and I thank all the other members of this research group in the period 1968-73 for their interest in my work: Dr. G. Kidd, Dr. P.R. McLean, D. Grangé, R.C. Meatherall, E.R. Farnworth, R. Lemanczyk, A. Van Putten, M. Danyluk and R. Judge.

I am very grateful to Mrs. Jan Coleman for her excellent work in typing this thesis.

This research was made possible through the financial assistance of the Department of Chemistry of McMaster University.

Finally, I thank my wife, Suzanne, who showed me where to look among the garbage and the flowers, and my daughter, Hillarie who showed me sweet innocence.
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INTRODUCTION

Molecular absorption spectra in the far ultraviolet (i.e., at wavelengths below 2000 Å) were first obtained by T. Lyman in the years between 1900 and 1914.

The first theoretical understanding of these spectra was provided at about the same time by N. Bohr, who suggested that optical spectra in atoms and molecules arise from the excitation of a valence electron to an orbit located mostly outside an ionic core. Bohr predicted that molecular absorption spectra should exhibit series of bands, with similar behaviour to atomic line spectra and which fit a Rydberg formula.

If \( \nu_n \) is the frequency of an absorption band in wavenumber units, labelled by a running number \( n \), and \( \nu_\infty \) is the frequency of the series limit, then Rydberg's formula is:

\[
\nu_n = \nu_\infty - \frac{R}{(n-\mu)^2}
\]

where \( R \) is called Rydberg's constant and \( \mu \) is approximately constant within a given series. Because the lines of the hydrogen spectrum fit the simplified Rydberg formula,

\[
\nu_n = \nu_\infty - \frac{R}{n^2}
\]

where \( n \) is the principal quantum number, \( \mu \) is called the quantum defect and represents the effect of the non-hydrogenic part of the ion-core.
Bohr's important work was followed by the identification of numerous Rydberg series in the absorption spectra of diatomic molecules such as H₂, N₂, CO and W.C. Price and co-workers found series in the polyatomic molecules H₂O, H₂S, CO₂, CS₂, CH₃I, C₆H₆ etc.

At the time of writing, Rydberg series have been identified in over 100 different molecules (see Reference 5 for a list to 1970) but a theoretical description of the electronic structure of Rydberg states in polyatomic molecules is far from complete; such a description is useful in understanding molecular excited states in general and is essential to the analysis and classification of Rydberg series in polyatomic molecules.

In this thesis a theoretical model is developed for the calculation of Rydberg terms in linear triatomic molecules and is applied to the analysis of Rydberg series in CO₂, CS₂ and CSe₂.
CHAPTER 1

Model Potentials and the Calculation of Atomic Rydberg Series

1.1 The Factorisation of Schrödinger's Equation for Excited States

M. Born and R.J. Oppenheimer have shown that a good approximation which greatly simplifies the mathematical description of molecular states is the separation of electronic and nuclear motions in the full molecular Schrödinger equation. This equation is:

\[ H(r_N, R, \theta, \phi) \psi_{\text{Mol}}(r_N, R, \theta, \phi) = E_{\text{Mol}} \psi_{\text{Mol}}(r_N, R, \theta, \phi) \]  \hspace{1cm} 1.1

where \( H \) is the Hamiltonian operator,
\( E \) is the total molecular energy,
\( r_N \) represents the 3N electronic co-ordinates
and \( R, \theta, \phi \) represent the molecular co-ordinates of internuclear separation and orientation.

The Born-Oppenheimer approximation leads to the factorisation of \( \psi_{\text{Mol}} \) into the product of an electronic function \( \psi_{\text{elec}}(r_N, R) \), a vibrational function \( \chi_{\text{vib}}(R) \), and a rotational function \( \theta_{\text{rot}}(\theta, \phi) \), i.e.:

\[ \psi_{\text{Mol}}(r_N, R, \theta, \phi) = \chi_{\text{vib}}(R) \theta_{\text{rot}}(\theta, \phi) \psi_{\text{elec}}(r_N, R) \]  \hspace{1cm} 1.2

Schrödinger's equation 1.1 can now be written in terms of an electronic wavefunction describing the motion of the electrons in the field of fixed nuclei.
where $E$ is the electronic energy.

The electronic Schrödinger equation 1.3 is usually solved by using the orbital approximation, in which the $N$ electrons are assigned $N$ one-electron functions $\psi_1, \psi_2, \ldots, \psi_N$ called orbitals.

$$
\psi_{\text{elec}}(r_1, r_2, \ldots, r_N, R) = \psi_1(r_1, R)\psi_2(r_2, R) \ldots \psi_N(r_N, R)
$$

A simplified form of the orbital approximation is particularly appropriate for the description of molecular states in which one electron is located mostly outside an ionic core.

The Born-Oppenheimer electronic Schrödinger equation for a molecule having $Q$ nuclei with position co-ordinates $R_a (a=1, 2, \ldots, Q)$ and nuclear charges $Z_a, Z_b, \ldots$ may be written,

$$
\begin{aligned}
\left(-\frac{1}{2} \sum_{k=1}^{N} \nabla_k^2 - \sum_{k=1}^{N} \sum_{a}^{Q} \frac{Z_a}{r_{ka}} + \sum_{i<k}^{N} \frac{1}{r_{ik}} + \sum_{a<b}^{Q} \frac{Z_a Z_b}{R_{ab}}\right) \psi_{\text{elec}} &= E \psi_{\text{elec}}
\end{aligned}
$$

If one electron is positioned well outside the remaining (core) electrons then one of the $r$'s, say $r_1$, is large compared to the others. In this case equation 1.5 may be written in the form,

$$
\begin{aligned}
\left(-\frac{1}{2} \nabla_1^2 &- \sum_{a}^{Q} \frac{Z_a}{r_{1a}} + \sum_{k=2}^{N} \frac{1}{r_{1k}} - \sum_{k=2}^{N} \frac{1}{2} \sum_{k=2}^{N} \frac{2}{r_{ka}} - \sum_{a<b}^{Q} \frac{Z_a Z_b}{R_{ab}}\right) \psi_{\text{elec}} &= E \psi_{\text{elec}}
\end{aligned}
$$
Since \( r_{1k} \) is large compared to all other \( r_{ik} \)'s, \( r_{1k} \) will be approximately the same for all \( k \) and,

\[
\sum_{k=2}^{N} \frac{1}{r_{ik}} = \frac{N-1}{r_{1}} \quad 1.7
\]

so that,

\[
\left\{ -\frac{1}{2} \nabla_{1}^{2} - \sum_{a} \frac{Qz_{a}}{r_{1}a} + \frac{N-1}{r_{1}} + \left[ -\frac{1}{2} \sum_{k=2}^{N} \nabla_{k}^{2} - \sum_{a} \frac{Qz_{a}}{r_{ka}} \right. \right. \\
\left. \left. \sum_{i=z<k}^{N} \frac{1}{r_{ik}} - \sum_{a<b} \frac{Qz_{a}z_{b}}{R_{ab}} \right] \psi_{\text{elec}} = E \psi_{\text{elec}} \right. 
\]

Upon separating the variables in equation 1.8 two equations are obtained, one describing the motion of the excited electron in the field of the molecular-ion represented by \( \psi_{\text{ex}} \) and the other defining the state of the molecular ion \( \psi_{\text{ion}} \), i.e.

\[
\psi_{\text{elec}}(r_{N,R}) = \psi_{\text{ex}}(r_{1,R}) \psi_{\text{ion}}(r_{N-1,R}) \quad 1.9
\]

and

\[
\left\{ -\frac{1}{2} \nabla_{1}^{2} - \sum_{a} \frac{Qz_{a}}{r_{1}a} + \frac{N-1}{r_{1}} \right. \psi_{\text{ex}}(r_{1,R}) = \varepsilon_{\text{ex}} \psi_{\text{ex}}(r_{1,R}) \quad 1.10a
\]

\[
\left\{ -\frac{1}{2} \sum_{k=2}^{N} \nabla_{k}^{2} - \sum_{a} \frac{Qz_{a}}{r_{ka}} \right. \right. \\
\left. \left. \sum_{i=2<k}^{N} \frac{1}{r_{ik}} - \sum_{a<b} \frac{Qz_{a}z_{b}}{R_{ab}} \right] \psi_{\text{ion}}(r_{N-1,R}) \right. \\
= \varepsilon_{\text{ion}} \psi_{\text{ion}}(r_{N-1,R}) \quad 1.10b
\]

The exactness of the product resolution described by equations 1.10a and 1.10b depends on the validity of the
approximation given by equation 1.7. J.C. Slater has shown that the error involved in equation 1.7 is

\[
\frac{N-1}{r_1} = \sum_{k=2}^{N} \frac{1}{r_{1k}} \sim \frac{R_{\text{ion}}}{r_1^2}
\]

where \( R_{\text{ion}} \) is the effective radius of the ion.

This means that equation 1.10a is a good approximation for excited electrons which have a high probability of being found at large distances from the ion core and \( \psi_{\text{ex}} \) is an exact representation of the wavefunction of the excited electron in the limit of \( r_1 \rightarrow \infty \). From equation 1.8 it can be seen that

\[
\frac{Q}{Z} \sum \frac{Z a}{r_{1a}} + \frac{Z}{r_1} \text{ as } r_1 \rightarrow \infty
\]

where \( Z \) is the sum of the nuclear charges and the asymptotic limit of equation 1.10a is

\[
\left( -\frac{1}{2} \nabla_1^2 - \frac{(Z-N+1)}{r_1} \right) \psi_{\text{ex}}(r_1) = \epsilon_{\text{ex}} \psi_{\text{ex}}(r_1)
\]

which is the equation of motion of an electron in a coulomb field due to a point charge \( Z-N+1 \). Hence an excited electron moves in a hydrogen-like potential at large \( r \).

This conclusion may also be reached from classical considerations of the coupling of angular momenta. At small \( r \) the orbital angular momentum \( \mathbf{l} \) is strongly coupled to the nuclear axis and the squared orbital angular momentum projection \( (\mathbf{l}_z)^2 \) is a constant of the motion. At large \( r \) on the other hand the electron experiences the isotropic coulombic attraction.
of an independently vibrating and rotating ion core, \( \hat{I} \) is
decoupled from the nuclear axis and \( \lambda \) is no longer defined.

1.2 The Atomic Effective Potential

In section 1.1 it was shown that the separation of the

electronic wavefunction \( \psi_{\text{elec}} \) into a product, \( \psi_{\text{ex}}(r_1, R)\psi_{\text{ion}}(r_{N-1}, R) \),
is valid only when the excited electron is classically at large
distances from the ion-core. At small distances the electron
repulsion term \( \sum_{i<k} \frac{1}{r_{ik}} \) introduces electron correlation and \( \psi_{\text{elec}} \)
cannot be separated. The separation can be maintained if
it is possible to construct an effective potential which is a
function of the co-ordinates of the excited electron only and
represents the average potential experienced by the electron
at any position in the ion field. Such an effective potential
shall be denoted by \( U(r) \) throughout this thesis. For atoms
\( U(r) \) constitutes a central field containing no angle dependent
terms and the electronic wavefunction is separable in spherical
polar co-ordinates.

\[
\psi_{\text{ex}}(r) = \psi(r, \theta, \phi) = R(r) Y_{\lambda}^{M}(\theta, \phi) \tag{1.12}
\]

The radial part of Schrödinger's equation for an electron
moving in a central field is:

\[
\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR(r)}{dr} + \left[ 2E - 2U(r) - \frac{i(i+1)}{r^2} \right] R(r) = 0 \tag{1.13}
\]

Putting

\[
P(r) = rR(r) \tag{1.14}
\]
in 1.13 gives
\[
\frac{d^2 P(r)}{dr^2} + \left[ 2E - 2U(r) - \frac{\ell (\ell + 1)}{r^2} \right] P(r) = 0
\]  

1.15

D.R. Hartree developed a numerical procedure for the determination of \( U(r) \) known as the method of self-consistent fields, but a much simpler semi-empirical approach first used by W. Heisenberg is to construct a "model potential" involving adjustable parameters which reproduce the observed eigenvalue spectrum. In constructing such a model potential it is useful to divide \( U(r) \) into two regions, one for small \( r \) and the other for large \( r \), where diverse physical environments prevail. The exact form of \( U(r) \) is known only in the asymptotic limit of large or small \( r \). Thus for an \( N \)-electron atom with nuclear charge \( Z_N \),

\[
U(r) \xrightarrow{r \to \infty} - \frac{(Z_N - N + 1)}{r} = - \frac{Z}{r}
\]  

1.16

and \( U(r) \xrightarrow{r \to 0} = - \frac{Z_N}{r} + C \)

where \( Z \) is the net charge on the ion-core and \( C \) is the constant potential arising from the core electrons.

\( U(r) \) Outside the Ion-Core

A Rydberg electron situated classically well outside an atomic ion-core experiences an essentially coulombic field except for polarisation corrections. These corrections arise because the Rydberg electron exerts an essentially homogeneous field \( - \frac{Z}{r^2} \) on the core and induces a dipole moment \( - \frac{a_d Z}{r^2} \) where
\( a_d \) is the dipole polarisability of the core. The potential energy due to the polarisation of the atom core is \( \frac{a_d z^2}{2r^4} \) and at large \( r \) this goes much more rapidly than the coulomb term and is usually neglected.

**U(r) Inside the Ion-Core**

The form of the Rydberg wavefunction is determined by the Pauli principle which requires that the wavefunction be orthogonal to all occupied core wavefunctions. This means that the nodes of the Rydberg wavefunction must be located at approximately the same radial distance as the antinodes of a core function with the same \( \ell \). If a Rydberg orbital has no real core precursors\(^1\) there are no orthogonality constraints on the form of the wavefunction inside the core. Such a Rydberg orbital is non-penetrating in the sense that the radial wavefunction is very small at small \( r \) and the boundary condition of these functions is practically the same as for hydrogen. Consequently the term values of non-penetrating Rydberg orbitals are close to the corresponding term values in hydrogen except for small polarisation corrections.

Penetrating Rydberg orbitals may be orthogonalized to the core wavefunctions by the method proposed by C. Herring\(^1\), who showed that the oscillations of the wavefunction produced by the orthogonality constraints in the core region could be reproduced by subtracting a suitable linear combination of core orbitals from a smooth function. In this case the Rydberg
function takes the form:

$$\psi_{\text{Ryd}} = \chi_{\text{Ryd}} - \sum_{c=1}^{N} a_c \phi_c$$  \hspace{1cm} (1.17)

where $\chi_{\text{Ryd}}$ is a non-orthogonal function and $\phi_c$ are the $N$ core eigenfunctions. The coefficients $a_c$ are chosen to make $\psi_{\text{Ryd}}$ orthogonal to the core orbitals $\phi_c$, i.e.

$$\langle \psi_{\text{Ryd}} | \phi_{\text{core}} \rangle = 0$$  \hspace{1cm} (1.18)

J.C. Phillips and L. Kleinman have shown that a function satisfying certain orthogonality constraints can be represented by an unconstrained function satisfying a modified Hamiltonian. The eigenvalue equation for a Rydberg electron is

$$H \psi_{\text{Ryd}} = E_{\text{Ryd}} \psi_{\text{Ryd}}$$  \hspace{1cm} (1.19)

where $\psi_{\text{Ryd}}$ is orthogonal to all core functions $\phi_{\text{core}}$. These core functions obey the eigenvalue equation,

$$H \phi_{\text{core}} = E_{\text{core}} \phi_{\text{core}}$$  \hspace{1cm} (1.20)

A function $\chi_{\text{Ryd}}$ which is non-orthogonal to the core orbitals will have the same eigenvalues as $\psi_{\text{Ryd}}$ when operated on by a modified Hamiltonian,

$$(H + V_R) \chi_{\text{Ryd}} = E_{\text{Ryd}} \chi_{\text{Ryd}}$$  \hspace{1cm} (1.21)

where $V_R$ represents a "pseudopotential" which takes account of the non-orthogonality of $\chi_{\text{Ryd}}$. From equations 1.19, 1.20, and 1.21 it is readily seen that
Because the core energies lie lower than the Rydberg energies, \( V_R \) behaves like a repulsive potential which largely cancels the coulomb potential inside the core. Hence the effective potential \( U(r) = -\frac{Z}{r} + V_R \) is probably small at small \( r \) except very close to the origin.

The pseudopotential formalism is inconvenient in practical applications because the pseudowavefunction \( \chi_{\text{Ryd}} \) is limited to the form of equation 1.17 which requires a knowledge of the core orbitals. Instead of remaining within the confines of pseudopotential theory many investigators have preferred to use simple model potentials from which model wavefunctions can be readily determined, and which require no knowledge of the core orbitals. The only restriction placed on the form of the model wavefunction is that it correctly reproduce the eigenvalue spectrum.

Many model potentials have been proposed in the literature, some of which have been suggested by pseudopotential theory. For example M.H. Cohen and V. Heine\(^{13}\) have suggested a simple cut off-coulomb potential,

\[
U(r) = \begin{cases} 
-\frac{Z}{r} & ; r > r_0 \\
0 & ; r < r_0 
\end{cases}
\]

\[1.23\]

in which \( r_0 \) is a variable parameter. I.V. Abarenkov and V. Heine\(^{14}\) proposed a more flexible two parameter potential,
\[ U(r) = -\frac{Z}{r}; \quad r > r_0 \]

\[ U(r) = A; \quad r < r_0 \]
in which A is a small constant. This particular model has proved to be successful in treating atomic and molecular Rydberg series and will be used in this thesis.

1.3 Solutions of the One-electron Schrödinger Equation for a Coulomb Field

Although many different atomic model potentials have been proposed they are all such that for \( r > r_0 \), a quantity of the order of the dimensions of the ion, the Rydberg wavefunction is one of the solutions of the equation:

\[ \frac{d^2 P_{n^*_i}(r)}{dr^2} + \left[ \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2} + 2E \right] P_{n^*_i}(r) = 0 \]

This equation constitutes a second order linear homogeneous differential equation and is an example of the Sturm-Liouville boundary value problem. The discrete spectrum of eigenvalues fit a Rydberg type formula,

\[ 2E = -\frac{Z^2}{n^*^2} \]

and it was pointed out by A. S. Eddington\(^1\) and Y. Sugiura\(^2\) that if the following substitutions are made in equation 1.25

\[ y = \frac{2Zr}{n^*}; \quad m = i + \frac{1}{2}; \quad P_{n^*_i}(r) = n^*_{i,m} \left( \frac{2Zr}{n^*} \right) \]

the equation of the confluent hypergeometric functions is obtained:
\[
d\frac{d^2 W_{n^*,m}}{dy^2} + \left[ \frac{n^*}{y} - \frac{1}{4} + \frac{\frac{1}{4} - m^2}{y^2} \right] W_{n^*,m} = 0
\]

1.28

These functions are discussed in detail in monographs by L. J. Slater\(^{17}\) and H. Buchholz\(^{18}\).

D.R. Hartree\(^{19}\) showed in an early paper on the Schrödinger radial equation that the general solution \(W_{n^*,m} (\frac{2Zr}{n^*})\) of equation 1.27 can be written in terms of a variable \(\sigma = 2Zr\) in the form:

\[
AW_{n^*,m} (\frac{2Zr}{n^*}) = G_\ell (\sigma) \cos n^* + H_\ell (\sigma) \sin n^*
\]

1.29

where \(G_\ell (\sigma)\) is the solution regular at the origin,

\[
G_\ell (\sigma) = \sigma^{i+1} \left[ a_0 + a_1 \sigma + a_2 \sigma^2 + \ldots \right]
\]

1.30

and \(H_\ell (\sigma)\) is the linearly independent solution irregular at the origin,

\[
H_\ell (\sigma) = \sigma^{i-1} \left[ b_0 + b_1 \sigma + b_2 \sigma^2 + \ldots \right] + a_0 G_\ell (\sigma) \log \sigma
\]

1.31

Both \(G_\ell (\sigma)\) and \(H_\ell (\sigma)\) can be represented by a power series in \(E\), and \(n^*\) by,

\[
n^* = n + a + \beta E + \gamma E^2 + \ldots
\]

1.32

This expansion which was first proposed by R.T. Birge\(^{20}\) contains the Rydberg and Ritz formulae if the series is terminated at the appropriate term.
An important special case of equation 1.25, known as
the zero energy Schrödinger radial equation has been studied
by G.H. Wannier. This equation is:
\[
\frac{d^2 \tilde{P}^*_{n^*} \ell(x)}{dr^2} + \left[ \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2} \right] \tilde{P}^*_{n^*} \ell(x) = 0
\]
1.33

By making the substitutions,
\[
v = \sqrt{8Zr} \quad \text{and} \quad \tilde{P}^*_{n^*} \ell = \frac{1}{2} \nu f(r)
\]
Bessel's equation of index \((2\ell+1)\) is obtained:
\[
\frac{d^2 f}{dv^2} + \frac{1}{v} \frac{df}{dv} + \left[ 1 - \frac{(2\ell+1)^2}{v^2} \right] f = 0
\]
1.34

The general solution of this equation is called a cylinder
function \(C_{2\ell+1}(v)\) which is an arbitrary linear combination of
Bessel functions of the first and second kinds, \(J_{2\ell+1}(v)\) and
\(Y_{2\ell+1}(v)\), i.e.
\[
f(r) = C_{2\ell+1}(v) = AJ_{2\ell+1}(v) + BY_{2\ell+1}(v)
\]
1.35

Wannier showed that providing \(4n^* \gg \sqrt{8Zr}\),
\[
\tilde{P}^*_{n^*} \ell(x) = \sqrt{8Zr} \left( J_{2\ell+1}(\sqrt{8Zr}) \cos n^* \frac{(n^*-\ell-1)\ell_{n^*}^{2\ell+1}}{(n^*+1)} + Y_{2\ell+1}(\sqrt{8Zr}) \sin n^* \right)
\]
1.36

Replacing \(n^*\) by \(n^* - \omega\) where \(\omega\) is the quantum defect at zero
energy and assuming the factor,
\[
\frac{(n^* - \ell - 1)!}{(n^* + \ell)!!} n^*^{2\ell + 1} = 1
\]
equation 1.37 reduces to:

\[
P_{n^* \ell} (r) = \sqrt{\frac{2}{\pi r}} \{ \cos \eta \psi J_{2\ell + 1}(\sqrt{2\eta \psi r}) - \sin \eta \psi Y_{2\ell + 1}(\sqrt{2\eta \psi r}) \}
\]

\( E \to 0 \)

Information on the physical meaning of the quantum defect can be obtained by considering the asymptotic behaviour of this equation. The asymptotic expansion of Bessel functions

\[
J_n(x), Y_n(x) \text{ is, for } x \text{ very large and } n \text{ small,}
\]

\[
J_n(x) \sim \left( \frac{2}{\pi x} \right)^{1/2} \cos \left( x - \frac{1}{2} n\pi - \frac{1}{4}\pi \right)
\]

\[
Y_n(x) \sim \left( \frac{2}{\pi x} \right)^{1/2} \sin \left( x - \frac{1}{2} n\pi - \frac{1}{4}\pi \right)
\]

With the substitution

\[
x - \frac{1}{2} n\pi - \frac{1}{4}\pi = \sqrt{2\eta \psi} - \frac{2\ell + 1}{2} \frac{1}{n\pi} - \frac{1}{4}\pi = \omega
\]

the asymptotic form of 1.38 is:

\[
R_{\nu \ell}^\text{Atom} (r) = \frac{P_{n^* \ell} (r)}{r} \sqrt{\frac{2}{\pi \sqrt{2\eta \psi}}} \left\{ \cos \eta \psi \cos \omega - \sin \eta \psi \sin \omega \right\}
\]

\( r \to \infty \)

or

\[
R_{\nu \ell}^\text{Atom} (r) \sim \frac{(8\eta)}{r^{3/4}} \sqrt{\frac{2}{\pi}} \cos (\omega + \eta \psi)
\]

Bethe and Salpeter have shown that the zero energy asymptotic form of the hydrogen functions \( R_{n \ell} (r) \), for which the field is coulombic all the way to the origin, is
\[ R_{\omega}^H (r) \sim \frac{\text{const}}{r^{3/4} \cos \omega} \]

Comparison of equations 1.41 and 1.42 shows that \( \pi \mu_{\infty} \) is the phase difference, \( \delta \), between the asymptotic solution of the radial equation for a potential which is coulombic all the way to the origin and the solution for a potential which departs from the coulomb form at small \( r \), i.e.

\[ \pi \mu_{\infty} = \delta \]

This result has also been proved by M.J. Seaton\(^{23}\) from a consideration of the zero energy form of continuum wavefunctions. Because the quantum defect is a slowly varying function of energy the relationship \( \pi \mu_{\infty} = \delta \) proved at zero energy will be a good approximation at small negative energies of the order of atomic Rydberg term energies. This suggests that the quantum defect may be obtained from a comparison of the relative phase of oscillation outside the ion-core of the actual wavefunction with energy \( E_n \) to a hydrogenic wavefunction with the same energy.

1.4 The Variation Principle and the Determination of Atomic Model Potentials

The problem of finding convenient general solutions of the one-electron radial Schrödinger equation for a coulomb field has received much attention from theorists since the pioneering work of Hartree and Wannier\(^{19,21}\). Tabulations of particular solutions are now available\(^{24}\) consisting of numerical
values of the regular and irregular coulomb functions evaluated by numerical integration techniques at given radial distances, \( r \), and energies \( E \). Solutions in this form are useful for matching boundary conditions inside and outside an ion core but do not provide convenient analytic functions which are appropriate for the calculation of entire Rydberg series.

Approximate eigenvalues and eigenfunctions of a differential equation may be obtained by setting up the corresponding variational problem. The one-electron Schrödinger equation to be solved may be written in the form:

\[
\hat{H} \Psi_i(r) = E_i \Psi_i(r)
\]

where \( \hat{H} \) is the Hamiltonian Operator,

\[
\hat{H} = \left\{ -\frac{1}{2} \frac{d^2}{dr^2} + U(r) + \frac{l(l+1)}{2r^2} \right\}
\]

The variational method requires the selection of a set of \( n \) linearly independent admissible functions \( \psi_i \) which constitute minimising sequences for the functional,

\[
Q = \frac{(\hat{H}\Psi, \Psi)_{\text{P}}}{(\Psi, \Psi)_{\text{P}}}
\]

If the \( \psi_i \) constitute a complete set then

\[
P = \lim_{n \to \infty} \sum_{i=1}^{n} C_i \psi_i
\]

and the same solution of 1.44 will be obtained irrespective of the particular functions chosen.

In practical applications of the variational method the size of the set of admissible functions is limited to a
finite number of terms and it is important to require that
the series converges rapidly to the exact wavefunction. The
convergence of a particular set is most rapid when the basis
functions $\Psi_i$ are themselves approximate eigenfunctions of $H$.

In the previous section it was shown that the solutions
of 1.44 are phase-shifted hydrogenic solutions and it is therefore
probable that the discrete hydrogen radial functions $P_{n\ell}(r)$
constitute a convenient orthonormal set with which to expand
the one electron atomic wavefunction $P_i(r)$. If this is the
case $P_i(r)$ will be given by,

$$P_i(r) = \sum_{n=1}^{N} c_{ni} P_{n\ell}(r)$$

where the $c_{ni}$ are expansion coefficients to be determined.
The hydrogen functions $P_{n\ell}(r)$ are given explicitly by the
equation:

$$P_{n\ell}(r) = \frac{(n-\ell-1)!2\ell!12}{n^2[(n+\ell)!]} \left( \frac{2\pi}{n} \right)^{\ell+1} e^{-Zr/n} \int_0^{2\pi} \frac{2\pi e^{-Zr/n}}{n+\ell} dr$$

and are the eigenfunctions of the radial Schrödinger equation:

$$H_{o}P_{n\ell}(r) = E_{n\ell}P_{n\ell}(r)$$

where

$$H_o = \left\{ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z^2}{r} + \frac{\ell(\ell+1)}{2r^2} \right\}$$

Equation 1.50 has eigenvalues given by,

$$E_{n\ell} = \int_0^{\infty} P_{n\ell}(r) H_{o}P_{n\ell}(r) dr = \frac{Z^2}{2n}$$
The energy eigenvalues of equation 1.44 are given by,
\[ E_i = \sum_{n} \sum_{n'} c_{ni} c_{n'i} H_{nn'} \]
where \( H_{nn'} \) is the matrix element:
\[ H_{nn'} = \int_0^\infty P_{nl}(r) H P_{n'l}(r) dr \]
If \( U(r) \) takes the form (c.f. Equation 1.24)
\[ U(r) = \begin{cases} \frac{Z}{r}; & r > r_o \\ -V_M; & r < r_o \end{cases} \]
substitution of 1.45 into 1.53 yields,
\[ E_i = \sum_{n} \sum_{n'} c_{ni} c_{n'i} \left[ \int_0^{r_o} P_{nl}(r) \left( -\frac{1}{r} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2} \right) P_{n'l}(r) dr \right. \]
\[ + \int_{r_o}^\infty P_{nl}(r) \left( -\frac{1}{r} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2} \right) P_{n'l}(r) dr \]
From which,
\[ E_i = \sum_{n} \sum_{n'} c_{ni} c_{n'i} \left[ \int_0^{r_o} P_{nl}(r) \left( \frac{Z}{r} - V_M \right) P_{n'l}(r) dr \right. \]
\[ + \int_{r_o}^\infty P_{nl}(r) \left( -\frac{1}{r} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2} \right) P_{n'l}(r) dr \]
The second integral in 1.57 contains the hydrogenic operator
\[ H_o \] (c.f. equation 1.51) so that,
\[ E_i = \sum_{n} \sum_{n'} c_{ni} c_{n'i} \left[ \int_0^{r_o} P_{nl}(r) \left( \frac{Z}{r} - V_M \right) P_{n'l}(r) dr + \delta_{nn'} E_i \right] \]
The expansion coefficients $c_{ni}$ are obtained by following the usual variational procedure of minimising $E_i$ as a function of all the $c_{ni}$. This leads to a set of $N$ linear simultaneous equations for the $c_{ni}$ which may be written in matrix notation:

$$Hc_i = c_i E_i$$

where $c_i$ is a column vector,

$$c_i = \{c_{i1}, c_{i2}, ..., c_{ni}, ..., c_{Ni}\}$$

$H$ may be diagonalized by a similarity transformation when the roots $E_i$ of $H$ are identical with the diagonal elements.

A programme was written in Fortran IV language for use on the McMaster University C.D.C. 6400 computer. A library matrix diagonalization subroutine was employed for the determination of the eigenvalues and eigenvectors. Once the model potential parameters $r_o$ and $V_M$ (Equation 1.58) were selected model Rydberg series were formed by arranging the calculated eigenvalues in order of decreasing energy. The lowest energy eigenvalue was assumed to correspond to the first member of a Rydberg series (i.e. the term with smallest $n^*$), and the number of higher series members calculated depended on the number of functions used in the expansion of the atomic wavefunction. Using 10 s-functions ($n=1, 2, ... 10$) or 9 p-functions ($n=2, 3, ... 10$) it was found that one Rydberg series could be calculated in ~4 sec C.P. time on the C.D.C. 6400 computer.
Results and Discussion

Two forms of the core model potential were investigated in this thesis. These were:

\[ V_M = A \quad ; \quad r < r_o \]

and

\[ V_M = - \frac{Z_C}{r} \quad ; \quad r < r_o \]

where \( A \) and \( Z_C \) are constants.

The form with \( V_M = A \) has been used in model potential calculations by A.U. Hazi and S.A. Rice\(^{25}\) and T. Betts and V. McKoy\(^{26}\). These authors determined an \( A \) value by setting equal at \( r_o \) the logarithmic derivatives of the wavefunction inside and outside \( r_o \). The calculations of these authors are not entirely satisfactory however because an arbitrary value of \( r_o \) was selected before an \( A \) value was determined by the curve matching procedure; a two parameter potential was thus limited to variation in one parameter. An optimum value of \( r_o \) was not determined and the question of the uniqueness of such a potential not discussed. These questions have been discussed in this work since the effect of varying both parameters \( A \) and \( r_o \) was investigated.

The above mentioned authors calculated Rydberg series in diatomic molecules using molecular model potentials constructed from superpositions of atomic model potentials. This method has been extended here to the calculation of Rydberg series in linear triatomic molecules and in particular to \( \text{CO}_2, \text{CS}_2 \) and \( \text{CSe}_2 \); for this purpose the atomic model potentials for the
atoms C, O, S and Se were required. Calculations were carried out for these atoms and the series obtained were compared to known Rydberg series taken from C.E. Moore's Tables of Atomic Energy Levels.²⁷

The work of Hazi and Rice and Betts and McKoy²⁵,²⁶ emphasizes that the model potential does not necessarily resemble the real potential in the core region but serves simply to parametrise the boundary conditions so that a model wavefunction with the same radial derivative as the actual wavefunction at \( r_o \) is obtained. For this reason it is not possible to equate the model radius \( r_o \) to any physical quantity such as the ionic radius, \( r_{\text{ion}} \). Nevertheless some correlation between \( r_o \) and \( r_{\text{ion}} \) may be expected and values of \( r_{\text{ion}} \) should enable approximate upper and lower bounds to be placed on acceptable values of \( r_o \).

Thus, for example, S.C.F. calculations²⁸ on \( 0^+ \) show that the radial charge distribution is essentially zero for \( r>4 \text{ a.u.} \) and \( \sim 90\% \) of the charge distribution is located at \( r<2 \text{ a.u.} \). For this reason \( r_o \) was restricted to values in the range 2-4 a.u. and an \( A \) value was determined which minimised \( \omega \) for each \( r_o \) where,

\[
\omega = \sum_{i}^{2} \left[ E_i^{\text{Calc}}(A, r_o) - E_i^{\text{Expt.}} \right]^2
\]

Calculated series are given for oxygen in Table 1.I. A number of interesting features of the results for oxygen will be discussed although many of the arguments can be generalized to the other atoms studied.
<table>
<thead>
<tr>
<th>Experimental Term Values (a.u.)</th>
<th>3s</th>
<th>4s</th>
<th>5s</th>
<th>6s</th>
<th>7s</th>
<th>8s</th>
<th>9s</th>
</tr>
</thead>
<tbody>
<tr>
<td>.15055</td>
<td>.06202</td>
<td>.03383</td>
<td>.02129</td>
<td>.01462</td>
<td>.01066</td>
<td>.00802</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated Term Values (a.u.)</th>
<th>A</th>
<th>( r_0 )</th>
<th>3s</th>
<th>4s</th>
<th>5s</th>
<th>6s</th>
<th>7s</th>
<th>8s</th>
<th>9s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-.020)</td>
<td>2.5</td>
<td>.15075</td>
<td>.06192</td>
<td>.03365</td>
<td>.02113</td>
<td>.01450</td>
<td>.01057</td>
<td>.00804</td>
<td></td>
</tr>
<tr>
<td>(-.160)</td>
<td>3.0</td>
<td>.15170</td>
<td>.06264</td>
<td>.03396</td>
<td>.02128</td>
<td>.01458</td>
<td>.01061</td>
<td>.00807</td>
<td></td>
</tr>
<tr>
<td>(-.210)</td>
<td>3.5</td>
<td>.15126</td>
<td>.06297</td>
<td>.03411</td>
<td>.02135</td>
<td>.01461</td>
<td>.01063</td>
<td>.00808</td>
<td></td>
</tr>
<tr>
<td>(-.225)</td>
<td>4.0</td>
<td>.15084</td>
<td>.06315</td>
<td>.03419</td>
<td>.02139</td>
<td>.01463</td>
<td>.01064</td>
<td>.00808</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zc ( r_0 )</th>
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<th>3.0</th>
<th>.15015</th>
<th>.06445</th>
<th>.03481</th>
<th>.02168</th>
<th>.01478</th>
<th>.01072</th>
<th>.00813</th>
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<tbody>
<tr>
<td>-425</td>
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<td>.15036</td>
<td>.06277</td>
<td>.03406</td>
<td>.02133</td>
<td>.01461</td>
<td>.01063</td>
<td>.00808</td>
<td></td>
</tr>
</tbody>
</table>
Table I. I shows that there exists a range of values of $A$ and $r_0$ over which good agreement can be obtained (i.e. to within 3% of the experimental term values). The $A$ and $r_0$ parameters which give the best fit to the oxygen $ns(^2S_o)$ Rydberg series are plotted in Fig. 1.I.

The arbitrariness of the model potential is accompanied by a corresponding arbitrariness in the expansion coefficients $c_{ni}$. The non-coulombic core serves to mix hydrogen radial functions of the same $l$ but different $n$ and the quantity $c_{ni}^2$ determines the amount of each hydrogen function, $P_{ni}(r)$, in the $i^{th}$ Rydberg A.O. with eigenvalue $E_i$. The calculation shows that $|c_{ni}|$ is largest for the hydrogen function with $n=i+1$ and $|c_{n=i+1,i}|$ increases with increasing $i$. The amount by which $c_{n=i+1,i}^2$ differs from unity measures the degree of "$n$-spoiling" and this varies with the best fitting parameters as shown in the Table I.II

<table>
<thead>
<tr>
<th>$r_0$ (a.u.)</th>
<th>$c_{21}^2$</th>
<th>$c_{87}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.814</td>
<td>0.964</td>
</tr>
<tr>
<td>3.0</td>
<td>0.781</td>
<td>0.956</td>
</tr>
<tr>
<td>3.5</td>
<td>0.767</td>
<td>0.953</td>
</tr>
<tr>
<td>4.0</td>
<td>0.762</td>
<td>0.949</td>
</tr>
</tbody>
</table>

Table II shows that the amount of $n$ spoiling decreases with increasing $n$, but is a function of the model potential.
Figure 1.1

Curve of Best-fitting parameters for oxygen
ns(\(^3S_o\)) Rydberg series
The amount of n spoiling is smaller when \( r_0 \) is smaller but is never more than 25% even for the largest \( r_0 \) used. Consequently the first s Rydberg orbital of an oxygen atom has considerable hydrogen 2s character. It should be emphasized however that this conclusion is not incompatible with the usual 3s designation of the lowest s-Rydberg level of oxygen. The designation 3s is made because the lowest possible Rydberg A0 of oxygen must have \( n_c-l \) innermost loops, where \( n_c \) is the number of occupied core precursors, plus one phase shifted hydrogenic outer loop giving a total of three loops. A model wavefunction does not reproduce the nodes or loops of the real one-electron wavefunction inside the core because, in the determination of the model wavefunction, the orthogonality constraints applying to the real one-electron wavefunction are replaced by a model (pseudo) potential which removes the oscillations of the real function inside the core; the model wavefunction is an accurate representation only of the largest loop of the real wavefunction which is situated outside the ion core. Our calculation shows that this outermost loop is somewhere between 75% and 82% hydrogen 2s like with smaller amounts of hydrogen 1s, 3s, 4s ... etc mixed in.

The 7% uncertainty in the exact form of the outermost loop arises from the corresponding uncertainty in the optimum choice of the parameters \( A \) and \( r_0 \). An ambiguity in the model potential parameters appropriate to a model wavefunction is to be expected when two quantities \((A \text{ and } r_0) \) are varied to obtain
agreement with one quantity, an energy eigenvalue. If unique model potential parameters are to be obtained a second quantity characteristic of the model wavefunction and dependent on the parameters must be found.

As we have seen variation of $A$ and $r_o$ changes not only the eigenvalue, $E_i$, but also the eigenvectors, $(c_{ni})$, of a model wavefunction. Changing the eigenvectors changes the relative amount of a particular hydrogen function in a model wavefunction and consequently changes $r_{max}$, the position of the radial maximum of the function. Unique values of model potential parameters could be determined if $A$ and $r_o$ were optimised not only to $E_i$ but also to $r_{max}$.

It may appear that $r_{max}$ is not a readily accessible quantity but the discussion on pp 14-16 shows that the quantum defect provides a connection between the energy of a Rydberg term and the phase-shift of a hydrogen function with the same energy. This suggests a convenient procedure for the determination of $r_{max}$ for any Rydberg A.O. which will be applied here to the case of an oxygen 3s term:

A hydrogen 3s function is,

$$R_{3s}^{H} (r) = N e^{-1/3r}(1 - 0.66667r + 0.074074 r^2)$$

and

$$E_{3s} = -\frac{1}{2x3^2} = -0.05556 \text{ a.u.}$$

An oxygen 3s term has energy $-0.15055$ a.u. and a hydrogenic function $R_{3s}^{O}(r)$ with the same energy is,
\[ R_{3s}'(r) = Ne^{-1/3(Zr)(1-0.66667(Zr) + 0.074074(Zr)^2)} \]

where

\[ E_{3s}' = -0.15055 = -\frac{2^2}{2\times3^2} \]

so that

\[ Z = 1.646 \]

Hence

\[ R_{3s}(r) = Ne^{-0.5487(1-0.0975r + 0.2007r^2)} \]

The function \( [R_{3s}'(r)]^2 r^2 \) has been plotted in Fig. 1.11 together with an hydrogen 3s function \([R_{3s}(r)]^2 r^2\). The curves show that \([R_{3s}'(r)]^2 r^2\) has the radial maximum of it's outermost loop situated at \( r=13.0 \) a.u., while \([R_{3s}'(r)]^2 r^2\) has this loop pulled in to \( r=8.0 \) a.u. The arguments presented on pp 14-16 indicate that the real one-electron oxygen 3s wavefunction behaves at large \( r \) like \( R_{3s}'(r) \) but with an inward phase shift of \( \pi \times 3_8 \) or 3.7 a.u. (See Equation 1.43). Thus the oxygen 3s wavefunction should have a radial maximum situated at \( r_{\text{max}}=8.0-3.7 \) or 4.3 a.u.

Before showing how knowledge of \( r_{\text{max}} \) enables a unique choice of \( A \) and \( r_0 \) to be made it will be shown that our estimated value of \( r_{\text{max}} \) for an oxygen 3s wavefunction is in good agreement with values of \( r_{\text{max}} \) obtained by two alternative methods:

1. H. Hosoya\(^{29}\) has calculated Rydberg orbitals for the atoms Li(I)-F(I) using linear combinations of Slater orbitals with exponents determined by energy and virial optimisation. Hosoya's Rydberg orbitals take the general form,
Fig. 1.11

Hydrogen 3s Function $R_{3s}(r)$ Compared with a Hydrogenic Function $R'_{3s}(r)$ Having the Same Energy as an Oxygen 3s Orbital
\[ R_{n\ell}(r) = \sum_{\alpha=1}^{n-\ell} c_{n\ell\alpha} S(\ell+\alpha, \mu_\alpha) \]

where \( S(n, \mu) \) is a Slater atomic orbital;

\[ S(n, \mu) = (2\mu)^{n+1/2} [(2\hbar) \lambda]^{-1/2} r^{n-1} e^{-\mu r} \]

For an oxygen 3s function Hosoya gives,

\[
R_{3s}(r) = 0.038125 S(1,7.7) - 0.045052 S(2,2.45) \\
+ 1.004047 S(3,0.645) - 0.119828 S(3,3.73)
\]

This function (see Fig. 1.III) has \( r_{\text{max}} = 4.65 \) a.u.

2. The procedure of Abarankov and Heine can be used in which the oxygen 3s wavefunction is plotted using tables of coulomb wavefunctions and the observed oxygen 3s term energy. The radial maximum of this function is 4.25 a.u. (See Fig. 1.III)

The use of values of \( r_{\text{max}} \) in obtaining unique values of \( \Lambda \) and \( r_0 \) can be seen from Fig. 1.III where oxygen 3s model wavefunctions, for two sets of parameters taken from table 1.I, are plotted together with Hosoya's oxygen 3s function and the coulomb wavefunction discussed in (2) above.

The curves show that the model wavefunction, which will be denoted \( \psi_{3s}(\Lambda, r_0) \), is smooth inside the ion core as expected from the discussion on p. 26. \( \psi_{3s}(\Lambda,4.0) \) has an \( r_{\text{max}} = 3.85 \) a.u. while \( \psi_{3s}(\Lambda,2.9) \) has \( r_{\text{max}} = 4.15 \) a.u. Our estimated value of \( r_{\text{max}} \) was 4.3 a.u. which shows that \( \psi_{3s}(\Lambda,2.5) \) is a better approximation to the real oxygen 3s wavefunction outside the core than \( \psi_{3s}(\Lambda,4.0) \).
Comparison of Model Wavefunctions with Other Wavefunctions

1. Hoťoja's Wavefunction, \( r_{\text{max}} \) (a.u.)
   \( 4.65 \)

2. Coulomb Wavefunction, \( 4.25 \)

3. Model Wavefunctions, \( \psi(A, 2.5) \)
   \( 4.15 \)

4. Model Wavefunctions, \( \psi(A, 4.0) \)
   \( 3.85 \)

---

The figure illustrates the comparison of model wavefunctions with other wavefunctions. The graph shows the spatial distribution of the wavefunctions, with curves labeled 1, 2, 3, and 4, each corresponding to different wavefunction sets.

- Curve 1: Hoťoja's Wavefunction, reaching a maximum at 4.65 a.u.
- Curve 2: Coulomb Wavefunction, with a maximum at 4.25 a.u.
- Curve 3: Model Wavefunctions, \( \psi(A, 2.5) \) at 4.15 a.u.
- Curve 4: Model Wavefunctions, \( \psi(A, 4.0) \) at 3.85 a.u.

The x-axis represents the radial distance in a.u., and the y-axis shows \( [R_{3s}(r)]^2 \cdot r \), indicating the probability density for the 3s state of a helium atom.
Unfortunately $r_{\text{max}}$ is not a very sensitive function of $r_0$ but the procedure outlined here indicates a useful method for estimating optimum values of $r_0$ with more certainty than any method of which the author is aware.
CHAPTER 2

Atomic Model Potentials and the Calculation of Molecular Rydberg Series

2.1 Introduction

In Chapter 1 it was shown that simple atomic model potentials can be used to reproduce accurately Rydberg term series in atomic spectra. We shall now investigate how these atomic model potentials may be used to calculate molecular Rydberg series. In going from the atomic to the molecular case we are naturally interested in what happens to atoms when they combine to form a molecule. This is an extremely complex question to which no simple answer can be given, but a useful start can be made on the problem by considering the two limiting cases of the united-atom and the separated atoms. In the former case the behaviour of the energies of the atomic orbitals is investigated when a "united-atom" nucleus, composed of all the nuclei in the molecule, is split to give slightly separated atoms, while in the latter case the effect of bringing together infinitely separated atoms to form a molecule is studied. Both of these approaches are useful in molecular calculations because the effects on atomic energy levels of slightly separating a united atom or bringing together infinitely separated atoms will be small and can be included as a perturbation to a Hamiltonian which contains purely atomic terms. In special cases the perturbation may be small
even at the equilibrium nuclear separation; the united-atom limit of small polyatomic hydrides such as \( \text{CH}_2, \text{H}_2\text{O}, \text{CH}_4 \) etc. is especially important in this respect.

In this chapter we shall use both the united-atom and separated atom concepts to investigate ways of using atomic model potentials for the calculation of molecular Rydberg series.

2.2 The United-Atom Approach

The positions of all the \( N \) nuclei in a molecule can be expressed in spherical polar coordinates \( R_i, \theta_i, \phi_i \) about an origin located at the centre of nuclear charge. If it is assumed that the electronic energy, \( E \), of the molecule is finite at all \( R_i \), \( E \) is an analytic function of the \( R_i \) and can be expanded in a convergent power series about \( R_i = 0 \) in powers of \( R_i 

\[
E = E_0 + \sum_i E_i R_i + \sum_{i<j} E_{ij} R_i R_j + \ldots \tag{2.1}
\]

The leading term, \( E_0 \), in equation 2.1 is referred to as the energy of the "united-atom" (i.e. the atom having atomic number \( Z = \sum_i Z_i \)), and the higher terms represent the effects of slightly separating the nuclei.

C. E. Wulfman has shown that the first non-zero terms of this expansion are quadratic in the nuclear separations and that there is a zero-order quadratic perturbation of united-atom one-electron states with the same energy and azimuthal quantum number \( i \). W. A. Bingel has given expressions
for the quadratic expansion coefficients in terms of the total electronic charge density of the united-atom and the charge density at the united-atom nucleus. However, these expressions require at least approximate united-atom core wavefunctions and are not suitable for use in model potential calculations.

Quadratic expansion coefficients have been evaluated without knowledge of united-atom core wavefunctions by H. Hosoya\textsuperscript{32} for the special case of non-penetrating Rydberg orbitals. In this case the molecular-ion core can be treated as a cluster of point charges with a specified geometry and the Rydberg orbital can be well approximated by a hydrogen orbital.

In order to include penetrating Rydberg orbitals in a calculation of this type the effect of the united-atom core must be taken into account. Our atomic model potential calculations demonstrate how this may be done for atoms and we shall now suggest a method by which these atomic calculations may be extended to a united-atom treatment of the Rydberg series of triatomic molecules.

Let us assume the united-atom appropriate to a linear triatomic molecule has Rydberg-term series with energies $E_i$ which can be represented by the eigenvalues of a model Hamiltonian,

$$H^0 \psi_i = E_i^0 \psi_i$$ 2.2
where $H^0 = T^0 + V^0$ with

$$
\psi^0 = \begin{cases} 
A & ; r < r_0^0 \\
\frac{-1}{r} & ; r \geq r_0^0
\end{cases}
$$

The $\psi_i$ are model Rydberg orbitals composed of linear combinations of hydrogen functions:

$$
\psi_i = \sum c_{ni} R_{n_l}(r) Y_{l}^{M}(\theta, \phi)
$$

The effect of splitting the united-atom to form a linear triatomic molecule, ABC, may be approximated by considering spheroidal deformations of the united-atom core with model radius $r_0$. The core will then be an ellipsoid governed by the equation:

$$
r(\theta) = r_0^0 (1 + a(\frac{3}{2} \cos^2 \theta - \frac{1}{2}))
$$

where $\theta$ is defined in Fig. 2.I and is such that,

$$
r(o) = a ; \quad r(\frac{\pi}{2}) = b
$$

$a$ and $b$ being the semi-major axes of the ellipse.

is related to the eccentricity $\varepsilon$ by:

$$
\varepsilon = \frac{a-b}{r_0^0} ; \quad a = \frac{2}{3} \varepsilon
$$

(1) **Outside the core**

We shall treat the deviation of the potential from a central field as a perturbation. Outside the ion core this will be:

$$
\Delta V_{\text{out}} = \left[- \frac{Z_A}{r_A^*} - \frac{Z_B}{r_B^*} - \frac{Z_C}{r_C^*} + \frac{1}{r_C^*} \right]
$$
Fig. 2.1

Co-ordinates for the United-Atom Calculation
For the special case of a symmetrical molecule with $Z_A = Z_B = Z$,

\[
\Delta V_{\text{out}} = 2Z \left[ \frac{1}{r_C} \frac{1}{r_A} \right]
\]

The first-order energy charge is:

\[
\Delta E_i = \int \psi_i \Delta V \psi_i \, dr
\]

so from equation 2.4

\[
[\Delta E_i]_{\text{out}} = 2Z \sum_{n n'} c_{n i} c_{n' i} \left[ \int_{r(\theta)} r C_i(R_C) \frac{1}{r_C} R_{n i}(r_C) r_C^2 dr_C \right.
\]

\[
- \int_{r(\theta)} r C_i(R_C) \frac{1}{r_A} R_{n i}(r_C) r_C^2 dr_C \left.ight]
\]

\[
\times \int \{ V, m(\theta, \phi) \}^2 \sin \theta \, d\theta \, d\phi \]

\[ R_{n i}(r) \] is a slowly varying function of $r$ in the range $r(\theta)$ to $r_C$. We shall assume the limit $r(\theta)$ can be replaced by $r_C$ without serious error.

The only integral in equation 2.11 not already evaluated in the atomic calculations (pp 17–20) is:

\[
I_A = \int_{r_C}^{r_C} R_{n i}(r_C) \frac{1}{r_A} R_{n i}(r_C) r_C^2 \{ V, m(\theta, \phi) \}^2 \sin \theta \, dr \, d\theta \, d\phi
\]

We shall consider the case of $p$-functions for which,

\[
I_A = \sum_{s=0}^{n-2} \sum_{t=0}^{n'-2} B_{n s} B_{n' t} (2s+1) \left( \frac{2}{n+1} \right) t+1 \Omega_{st}
\]
where

\[ N = \sqrt{\frac{4(n-2)1}{n^4 (n+1)!}} \]  \hspace{1cm} 2.14

and the \( B_{ns} \) are expansion coefficients for the Laguerre polynomials occurring in \( R_{n\ell}(r) \).

\[ Q_{st} \] is the integral left to be evaluated:

\[ Q_{st} = \int r_C^{s+1} e^{-r_C/n} r_A^{t+1} e^{-r_A/n} \left\{ \begin{array}{l} \cos^2 \theta \\ \sin^2 \theta \cos^2 \phi \end{array} \right\} \mathrm{d}t \]  \hspace{1cm} 2.15

with \( \alpha_n = \frac{1}{n} \) and \( \beta_n = \frac{1}{n} \).

\[ Q_{st} = (-1)^{s+t} \frac{\alpha_n^{s+t}}{\beta_n} Q_{00} \]  \hspace{1cm} 2.16

If \( Q_{00} \) is known, \( Q_{st} \) can be determined using this equation.

\( Q_{00} \) was evaluated by a transformation to elliptical coordinates as shown in Fig. 2.2. Elliptical coordinates are defined by the equations:

\[ u = \frac{r_C + r_A}{R} \hspace{1cm} v = \frac{r_C - r_A}{R} \hspace{1cm} \phi = \phi \]  \hspace{1cm} 2.17

\[ 1 \leq u \leq \infty \hspace{1cm} -1 \leq v \leq 1 \hspace{1cm} 0 \leq \phi \leq 2\pi \]

\[ d = \frac{R^3}{\beta} (u^2 - v^2) \mathrm{d}u \mathrm{d}v \mathrm{d}\phi \]  \hspace{1cm} 2.18

After evaluation:

\[ [Q_{00}]_{\beta} = \frac{\pi R^4}{8} \left\{ \frac{1}{15} [10 C_3(a,u) + 16 C_1(a,u)] \right\} \]  \hspace{1cm} 2.19a
Co-ordinate Transformation for United-Atom Calculation

Fig. 2.11
and,

\[ [Q_{00}]_{p,n} = \frac{\pi R^4}{8} \left\{ \frac{1}{15} \{ 10 C_3(a,u) - 8 C_1(a,u) \} \right\} \]

where

\[ C_n(a,u) = \int_0^\infty x^n e^{-ax} \frac{dx}{\mu} = e^{-au} \sum_{k=0}^{n!} \frac{u^k}{k!} \frac{n!}{a^{-k+n}} \]

with \( a = \frac{R}{2} \left( \frac{1}{n} + \frac{1}{n^2} \right) \)

\[ \mu + \nu = \frac{2r_c}{R} = u \]

A computer programme was written using equations 2.12-2.21 for the evaluation of \( I_A \). \( I_A \) values were checked by numerical integration using a 72-point Gaussian quadrature programme.

(ii) Inside the core

If the difference between the potentials of the deformed and undeformed core is \( \Delta V_{in} \) we have,

\[ r_c^2 \sin \delta d \delta d \]

\[ [E_1]_{in} = \sum \sum c_n c_{n'} \int r_n'(r_c) \Delta V_{in} r_{n'}(r_c) \{ Y_{i,m(\theta,\phi)} \} \]

\[ r_c^2 \sin \delta d \delta d \]

\[ [E_1]_{in} \] may be evaluated by following the closely related theory of deformed nuclei given by H. Kopfermann. \(^{34}\) \( R_{ni}(r) \) is a slowly varying function of \( r \) and can be taken outside the integral over \( r_c^2 \sin \delta d \delta d \)

\[ [E_1]_{in} = \sum \sum c_n c_{n'} \int r_n'(r_c) r_{n'}(r_c) \{ Y_{i,m(\theta,\phi)} \} \]

\[ r_c^2 \sin \delta d \delta d \]

\[ [E_1]_{in} = \sum \sum c_n c_{n'} \int r_n'(r_c) r_{n'}(r_c) \{ Y_{i,m(\theta,\phi)} \} \]

\[ r_c^2 \sin \delta d \delta d \]
where $A$ is the united-atom core potential.

From equations 2.5 and 2.7, neglecting terms in $\varepsilon^2$ and $\varepsilon^3$ (i.e. for small deformation):

$$[\Delta E_i]_{\text{in}} = \frac{A e (r_c^0)^3}{3} \sum_{n} \frac{1}{n} \sum_{n'} \frac{1}{n'} \sum_{l} \sum_{l'} \frac{1}{r_{nl}} \frac{1}{r_{n'l'}} \frac{1}{r_{c'l}} \frac{1}{r_{c'l'}} I_{ll'} 2.24$$

where

$$I_{ll'} = \int 2 \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \{Y_{l,m}(\theta, \phi)\}^2 \sin \theta \, d\theta \, d\phi 2.25$$

The integral $I_{ll'}$ is related to the quadrupole moment of the deformed core and is well known in the theory of angular momentum. Explicitly,

$$I_{ll'} = \frac{l(l+1) - 3m^2}{(2l-1)(2l+3)} 2.26$$

Hence for $p\sigma$ and $p\pi$ orbitals,

$$I_{p\sigma} = \frac{2}{5} ; \quad I_{p\pi} = -\frac{1}{5} 2.27$$

The formulae derived in the previous pages were used to construct computer programmes for the evaluation of $[\Delta E_i]_{\text{in}}$ and $[\Delta E_i]_{\text{out}}$. The calculation was applied to particular molecules with the assumption of maximum charge separation ($Z_A = 1, Z_B = \frac{1}{2}$, $Z_C = 0$) and $\varepsilon$, the eccentricity of the ellipsoid, was left as an unknown quantity to be determined by comparison with experimental data.

As we have mentioned previously (p.34) the united-atom approach is especially useful for the description of hydrides.
of the type $XH_n$. Unfortunately np-Rydberg series in linear
$XH_2$ molecules (e.g. $CH_2$) are not well established, but np
series are well known for bent $XH_2$ molecules in general, and
for $H_2O$ in particular.

A $p$ orbital centred on the $X$ atom of a bent $XH_2$
molecule will transform like either an $a_1$, $b_1$ or $b_2$ representation
of the $C_{2v}$ point group. The $pa_1$ and $pb_2$ orbitals may be formed
from suitable combinations of the $p\sigma$ and $p\pi$ orbitals appropriate
to linear $XH_2$, but the $pb_1$ orbital is identical with the $p\pi$
orbital of linear $XH_2$. Consequently the formulae we have
derived for np$\pi$ orbitals in linear $XH_2$ can be applied to npb$\pi$
orbitals in bent $XH_2$.

Calculations were carried out on the npb$\pi$ Rydberg series
of $H_2O$ using the united-atom Ne described by a model potential
with $A = -0.38$ and $r^0 = 2.5$ a.u. Calculated series were
compared with experimental series tabulated by T.F. Lin and
A.B.F. Duncan. The optimum $\varepsilon$ value for the core (see equation
2.24) was found to be $0.12$. $AE$ values are given in Table 2.1 with

$$E_{tot} = \Delta E_{out} + \Delta E_{in}$$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\Delta E_{out}$ (a.u.)</th>
<th>$\Delta E_{in}$ (a.u.)</th>
<th>$\Delta E_{tot}$ (a.u.)</th>
<th>$E_{tot}$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.00701</td>
<td>0.00447</td>
<td>0.01148</td>
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<tr>
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</tr>
<tr>
<td>5</td>
<td>0.00092</td>
<td>0.00090</td>
<td>0.00182</td>
<td>0.00178</td>
</tr>
</tbody>
</table>
Discussion

The quantum defect for a molecular Rydberg series, $\mu_{\text{Mol}}$, can be divided into two parts:

$$\mu_{\text{Mol}} = \mu_{\text{pen}} + \mu_{\text{c.s.}}$$

$\mu_{\text{pen}}$ is an atomic-like term arising from the spherical, but non-coulombic, contributions to the potential inside the core while $\mu_{\text{c.s.}}$, where c.s. stands for core-splitting, is a strictly molecular term representing the effects of the non-spherical part of the potential field inside and outside the core.

In the model potential calculations presented here, $\mu_{\text{pen}}$ can be determined from the model potential of the united-atom and we have also shown how the molecular term $\mu_{\text{c.s.}}$ can be estimated.

In view of the approximate nature of our united-atom model the conclusions to be drawn from this calculation are probably only of a rough quantitative nature. Nevertheless the model does give useful information on the origin of the symmetry splittings in $\text{XH}_2$ molecules and thereby the relative contributions to c.s. from inside and outside the ion core. Thus while it is well established that the radial maximum of a molecular Rydberg wavefunction is located well outside the ion core, our calculation shows that about one-half of the energy level splittings due to the non-spherical part of the potential comes from Rydberg electron density inside the ion core. Similar conclusions have been reached for p series in $\text{H}_2$ by G. Herzberg and C. Jungen [37].
Evidently this surprising result comes about because the deviation of the potential from a central field is much larger inside the ion core than well outside, and apparently this is more important than the fact that the probability of finding the Rydberg electron inside the core is very small.

2.3 The Separated Atom Approach

(i) General Discussion

The results of Section 2.1 show that model potential calculations of molecular Rydberg series can be successful only if an accurate representation of the ion-core potential is used. A united-atom model is restricted in practical applications to hydride molecules and we shall therefore consider the more useful separated atom approach in greater detail. We shall show how a model potential applicable to any molecule can be constructed from combinations of separated atom model potentials and discuss the use of these models in calculating Rydberg series in linear triatomic molecules.

In order to bring out the important features of separated atom model potential calculations we shall first develop the theory for a diatomic molecule AB, and then show how it may be extended to polyatomic molecules.

Consider a Rydberg electron moving in the field of a spherical core A with residual charge $Z_A$, and suppose the observed eigenenergies $E_A(n\ell)$ of the Rydberg states can be reproduced by a model potential $V_A(r_A)$. The formation of a molecule can be imagined by bringing up a second atom B with Rydberg energies $E_B(n\ell)$ described by a model potential $V_B(r_B)$. 
The combined system is governed by the one-electron Schrödinger equation:

\ [-\frac{1}{2} \nabla^2 + V_A(r_A) + V_B(r_B) + V_{AB}(R) - E_k(R)] \psi_k = 0 \tag{2.28} \]

where \( \psi_k \) is the wavefunction of the Rydberg electron with energy \( E_k \). \( V_{AB}(R) \) represents the effects of bonding interactions between the two cores separated by a distance \( R \). This interaction takes the form:

\[ V_{\text{Bonding}} = \sum_{i=A} \sum_{j=B} \left( \frac{1}{r_{ij}} - \frac{Z_A}{r_{Aj}} - \frac{Z_B}{r_{Bi}} \right) \] \tag{2.29}

where \( i=A \) represents a summation over all the electrons associated with atom A etc.

Diatomic molecules such as Li\(_2\) and Na\(_2\) have large equilibrium nuclear separations and it is valid to assume that the core electrons do not contribute to the binding of the molecule.\(^{38,39}\) In this case \( V_{AB}\rightarrow 0 \) except for small polarisation terms \( (\frac{1}{r}) \). The (weak) binding in these molecules is due to the Rydberg electron moving in the potential field of the two atomic ion cores. For most diatomic molecules, however, the binding arises from an overlapping of the two cores when \( R_{\text{eqilb}} \) is less than the sum of the core radii of the constituent atoms and \( V_{AB}\rightarrow 0 \).

In view of the complex form of \( V_{AB} \) a number of molecular model potential calculations have been carried out in which \( V_{AB} \)
is ignored completely\textsuperscript{25,26,40}. Certainly the neglect of $V_{AB}$ is a valid first approximation because the interatomic interactions which $V_{AB}$ represent are much smaller than the intra-atomic interaction terms $V_A$ and $V_B$. The effects of ignoring $V_{AB}(R)$ will be discussed later in this chapter.

(ii) Model Potentials for Polyatomic Molecules

The discussion of the previous pages suggests that, for any polyatomic molecule, the potential in which a Rydberg electron moves can be constructed from a sum of atomic contributions:

$$V_{\text{Mol}} = \sum_i V_i(r_i) \quad \text{2.30}$$

In this thesis the $V_i$ are represented by the atomic model potentials discussed in Chapter 1. Each atom $i$ has a core region bounded by a sphere of radius $r_i^0$ centred at the $i$th nucleus. Inside the core the potential is a constant, $A_i$, and outside the core the potential is coulombic and depends on the partial charge $\delta Z_i$ to be associated with the atom $i$. Thus:

$$V_i = \begin{cases} Z_i & r_i > r_i^0 \\ A_i & r_i \leq r_i^0 \end{cases} \quad \text{2.31}$$

If the molecular core has a net charge $Z_C$ then,

$$Z_C = \sum_i \delta Z_i \quad \text{2.32}$$
This molecular model was proposed by A.U. Hazi and S.A. Rice and used for the calculation of Rydberg series in diatomic molecules by these authors and also by T. Betts and W. McKoy. However, as we pointed out previously (p.21), both of these authors used arbitrary values of \( r^0 \) and the uniqueness of their calculated Rydberg series is questionable. In Chapter 1 it was shown that the ambiguity in the optimum values of the model parameters \( A \) and \( r^0 \) can be eliminated by comparing the model wavefunctions to phase-shifted hydrogen functions to ensure the correct asymptotic behaviour of the model wavefunction.

(iii) The Model Potential for \( \text{CO}_2 \)

In order to calculate Rydberg series for \( \text{CO}_2 \) optimum atomic model potentials for carbon and oxygen were obtained and it was found that the \( r^0 \) values for these atoms fall in the range 2.0-2.5 a.u.. The final selection of exact \( r^0 \) values for carbon and oxygen was based on the observation that the C-O bond length of 2.22 a.u. found in the ground state of \( \text{CO}_2^+ \) lies in the range of optimum \( r^0 \) values for these atoms. In addition it was found that allowing the model radius of one atom to pass through the nucleus of the adjacent atom (i.e. setting \( r^0 \) equal to the bond length) greatly simplified the evaluation of certain integrals important to the calculation of \( \text{CO}_2 \) Rydberg series. For this reason the \( r^0 \)'s used in calculations on \( \text{CO}_2 \) were chosen as follows:

\[
\begin{align*}
  r^0_c &= r^0_o = r^0_{\text{CO}_2}^+ (\text{C-O}) = 2.22 \text{ a.u.} \\
\end{align*}
\]

where \( r^0_c \) is the \( r^0 \) for carbon,
\( r^0_o \) is the \( r^0 \) for oxygen.
Calculated charge distributions for CO$_2$ indicate that the selection of the same model radius for carbon and oxygen is probably a good approximation.

(iv) **The Model Potentials for CS$_2$ and CSe$_2$**

R.F.W. Bader et al. studied the charge distributions of CO$_2$, CS$_2$ and OCS and in particular the changes occurring in the charge population about the carbon atom as the bonding environment is changed. Their conclusions indicate that $r_c^O$, the model radius for carbon, should remain essentially unchanged in going along the series CO$_2$, CS$_2$, CSe$_2$. Hence, in constructing $V_{\text{Mol}}$ for CS$_2$ and CSe$_2$, we set $r_c^O$ equal to the same value as $r_c^O$ in CO$_2$ and, in keeping with the $V_{\text{Mol}}$ chosen for CO$_2$, $r_s^O$ and $r_{\text{Se}}^O$ were set equal to $r_{\text{CS}_2^+}$ (C-S) and $r_{\text{CSe}_2^+}$ (C-Se) respectively.

A schematic cross-sectional representation of the model potentials used for CO$_2$ and CS$_2$ is given in Fig. 2.III.

**Table 2.II**

<table>
<thead>
<tr>
<th>Atomic Model Potential Parameters used in the Calculation</th>
<th>Rydberg Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>of CO$_2$, CS$_2$ and CSe$_2$</td>
<td>C</td>
</tr>
<tr>
<td>$r_c^O$ (Å)</td>
<td>2.196</td>
</tr>
<tr>
<td>$r_s^O$ (Å)</td>
<td>1.10</td>
</tr>
<tr>
<td>$r_{\text{Se}}^O$ (Å)</td>
<td>-0.14</td>
</tr>
</tbody>
</table>
Fig. 2.III

Model Potentials for CO$_2$ and CS$_2$
2.4 Expansion of the Molecular Rydberg Wavefunction

In order to calculate molecular Rydberg series we must look for a suitable expansion of the Rydberg wavefunction to use in conjunction with the molecular model potentials described in section 2.3.

Consider the case of a Rydberg electron moving in the field of a linear symmetric $\text{XY}_2^+$ ion core. If there is a maximum separation of the net charge on the ion, the Rydberg electron moves in a field which is indistinguishable from that of the diatomic ion $X_2^+$ outside the core.

R.S. Mulliken\textsuperscript{10,42} has pointed out that the MO's of $\text{H}_2^+$ serve as useful prototypes for the Rydberg MO's of homonuclear diatomic molecules because these MO's behave asymptotically like phase-shifted $\text{H}_2^+$ MO's. We therefore expect a knowledge of $\text{H}_2^+$ wavefunctions to be useful in understanding the nature of Rydberg MO's in the same way that hydrogen functions are used as a starting point in the study of atomic Rydberg orbitals.

The wavefunctions of $\text{H}_2^+$ have been studied in detail by D.R. Bates et. al.\textsuperscript{43}. The one-electron Schrödinger equation for $\text{H}_2^+$ is separable in confocal-elliptical coordinates:

![Figure 2.1V](image)

$H_2^+$ co-ordinates
\[ n = (r_A - r_B) \frac{R}{2} \quad ; \quad \lambda = (r_A + r_B) \frac{R}{2} \]  \hspace{1cm} 2.33

\[ \psi(r_A, r_B, R) = E(R) \psi(r_A, r_B, R) \]  \hspace{1cm} 2.34

\[ \psi(r_A, r_B, R) \xrightarrow{\text{Transform to Elliptical co-ords}} \psi(\lambda, \mu, \phi) = \Lambda(\lambda) M(\mu) \phi(\phi) \]  \hspace{1cm} 2.35

Separation of the variables \( \lambda, \mu \) and \( \phi \) leads to three equations:

\[ \phi(\phi) = \begin{pmatrix} \cos \mu \\ \sin \mu \end{pmatrix}(m\phi) \]  \hspace{1cm} 2.36

\[ \frac{d}{d\mu} \left\{ (1-\mu^2) \frac{du}{d\mu} \right\} + \left\{ -A + p^2 \mu^2 - \frac{m^2}{1-\mu^2} \right\} u = 0 \]  \hspace{1cm} 2.37

\[ \frac{d}{d\lambda} \left\{ (\lambda^2-1) \frac{dA}{d\lambda} \right\} + \left\{ A + 2R\lambda - p^2 \lambda^2 - \frac{m^2}{\lambda^2-1} \right\} A = 0 \]  \hspace{1cm} 2.38

where \( p, A' \) and \( m \) are separation constants with,

\[ p^2 = -\frac{1}{4} R^2 E \quad \text{and} \quad A' = A - p^2 \]  \hspace{1cm} 2.39

It can be shown that the operators \( H, A' \) and \( L_z \) form a complete set of commuting observables for \( H_2^+ \) and therefore provide a classification of the stationary states of the system.

In the limit of \( R \to 0 \),

\[ \Lambda(\lambda) \to R_{ni}(r) \]  \hspace{1cm} 2.40

and

\[ M(\mu) \to P_{\mu}^m(\cos \phi) \]
where the \( R_{n\ell}^k(r) \) are hydrogen radial functions and the \( P_{\ell}^m(cos\phi) \) are associated Legendre functions and are part of the hydrogen angular functions.

Because \( H_2^+ \) functions are asymptotically separable in spherical polar co-ordinates, the behaviour of \( H_2^+ \) wavefunctions near the united-atom limit is similar to their behaviour at very large \( r \). At small \( R \),

\[-A' = \ell(\ell+1) \tag{2.41}\]

and consequently \( H_2^+ \) Mo's are hydrogenic in their outermost parts with well defined \( \ell \) values.

At smaller \( r \) the non-spherical part of the potential introduces a quadrupolar field which couples states of different \( \ell \) and only the \( \phi \) dependent factor of the wavefunction remains the same as in hydrogen. Nevertheless calculations show that even for the lowest excited \( H_2^+ \) orbitals the \( \ell \)-purity is quite high and the wavefunctions are still at least approximate eigenfunctions of \( \ell \). It is for this reason that \( H_2^+ \) Mo's are usually classified according to their united-atom designation.

The \( \ell \)-purity of \( H_2^+ \) wavefunctions can be estimated using the eigenfunctions \( M(\mu) \) which are usually expanded in terms of the associated Legendre polynomials:

\[ M(\mu) = \sum_s f_s(\ell, m, p) P_{m+s}^m(cos\phi) \tag{2.42} \]

and \( \lim_{R \to 0} \mu = \cos\theta \).
The summation in 2.42 is over even values of $s$ if $(l+m)$ is
even and over odd values of $s$ if $(l+m)$ is odd. D.R. Bates has
has tabulated values of the coefficients $f_s(l, m, p)$ for many
states of $H_2^+$ as a function of the internuclear separation
$R$. We have used these coefficients as an approximate measure
of the $l$-purity of states for CO$_2$. With a maximum charge
separation on the CO$_2^+$ point ion core the Rydberg electron
at large $r$ moves in the field of a $H_2^+$-like system with
$R=4.4$ a.u. and charge $Z=\frac{1}{2}$ on each nucleus. The coefficients
$f_s'$ ($f_s$ normalised to 100) for this system are given in table 2:III.

Table 2:III shows that at least 90% of the angular
part of the wavefunction is composed of terms with an $l$ value
appropriate to the $l$ value of a united-atom designation, and
this percentage increases with increasing $n$. Furthermore, if
more terms are required to secure a good approximation to
the wavefunction only a few will be needed because the $l$ series
are rapidly convergent.

<table>
<thead>
<tr>
<th>United-Atom Designation</th>
<th>$f_0'$</th>
<th>$f_1'$</th>
<th>$f_2'$</th>
<th>$f_3'$</th>
<th>$f_4'$</th>
<th>$f_5'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2s_{1g}$</td>
<td>91.2</td>
<td>0.0</td>
<td>8.7</td>
<td>0.0</td>
<td>~0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$3s_{1g}$</td>
<td>95.4</td>
<td>0.0</td>
<td>4.5</td>
<td>0.0</td>
<td>~0.04</td>
<td>0.0</td>
</tr>
<tr>
<td>$2p_{1u}$</td>
<td>0.0</td>
<td>93.8</td>
<td>0.0</td>
<td>6.1</td>
<td>0.0</td>
<td>~0.1</td>
</tr>
<tr>
<td>$3p_{1u}$</td>
<td>0.0</td>
<td>97.6</td>
<td>0.0</td>
<td>2.3</td>
<td>0.0</td>
<td>~0.02</td>
</tr>
</tbody>
</table>
From the tabulated values of \( f_s \) it may be estimated that there will be less than 10% s-d mixing in the lower ns\(_g\) orbitals of CO\(_2\) and less than 7% p-f mixing in the lower np\(_u\) orbitals. However while this means that the maximum error in any CO\(_2\) wavefunction calculated without \( f \)-spoiling is probably \( \approx 10\% \), the corresponding error in the calculated term energy is certainly much smaller than this. This is because of a well-known property of variationally determined wavefunctions\(^{46}\). If \( \phi \) is an approximation to an exact one-electron wavefunction \( \phi_n \) with error \( \Delta \phi \), the corresponding error in the energy \( \Delta E \) is \( O(\Delta \phi)^2 \). In other words a variational wavefunction good to 10% may give an energy good to 1%.

2.5 The Calculation of Rydberg series in Linear Triatomic Molecules Using a Separated Atom Model

(i) Procedure

The discussion of section 2.4 indicates that the Rydberg orbitals of linear triatomic molecules are very similar to united-atom functions outside the ion-core. Model wavefunctions are not intended to reproduce the precise form of one-electron functions inside an ion core; all that is required is that the combined system of model wavefunction and model potential give the correct relative contributions to the quantum defect from inside and outside the ion core. Since our molecular model potential is constructed from the separated atoms it may be expected that separated atom wavefunctions, \( S\_A \), must be used.
for the inner parts of the Rydberg wavefunction where,

$$\psi_{\text{S.A.}} = \chi_A + \chi_B + \chi_C + \ldots$$

and $\chi_A, \chi_B, \chi_C \ldots$ are functions located at the nucleus of the atoms A, B, C \ldots etc. However, it appears that united atom functions can also be used inside the molecular ion core. Thus Tien Chi Chen\textsuperscript{47} has shown that even in the case of the ground state of $H_2^+$ \approx 90\% of the $1s\sigma_g$ energy is due to contributions of spherical functions located at the molecular mid-point.

Hence, in this section, single centre expansions of linear triatomic Rydberg orbitals will be used. The effects of expanding Rydberg wavefunctions in $CO_2$ about two centres in the molecule will be discussed in Section 2.6.

Consider the case of a linear molecule a-b-c\ldots. The Schrödinger equation for an electron in a Rydberg orbital $\psi_k$ is:

$$\left[-\frac{1}{2} \nabla^2 + \sum_i V_i(r_i)\right] \psi_k(r_q) = E_k \psi_k(r_q) \quad 2.43$$

where the Rydberg orbital is centred on the nucleus of atom q.

As previously $\psi_k$ will be represented by a linear combination of hydrogen functions $\zeta_{n\kappa}$ centred on q.

$$\psi_k(r_q) = \sum_{n=1}^{N} c_{n\kappa} \zeta_{n\kappa}(r_q) \quad 2.44$$

Equations 2.43 and 2.44 lead to matrix elements $H_{nn'}$, given by,

$$H_{nn'} = \int c_{n\kappa}(r_q) \left[-\frac{1}{2} \nabla^2 + V_q(r_q) + \sum_i V_i(r_i)\right] \zeta_{n'\kappa}(r_q) \, dr_q \quad 2.45$$
or,

\[ H_{nn'} = \phi_{n q}(r_q) [H + V_q(r_q) + \frac{1}{r_q} + \sum_{i \neq q} \frac{V_i(r_i)}{i} \phi_{n'i}(r_q) d_{i q} ] \]

where \( H_0 \) is the hydrogenic Hamiltonian Operator.

Hence,

\[ H_{nn'} = \delta_{nn'} E_n + \phi_{n q}(r_q) [V_q(r_q) + \frac{1}{r_q} + \sum_{i \neq q} \frac{V_i(r_i)}{i} \phi_{n'i}(r_q) d_{i q} ] \]

The \( E_n \) are hydrogen eigenenergies in a.u.,

\[ E_n = -\frac{1}{2n^2} \]

Equation 2.47 shall be written in the form:

\[ H_{nn'} = \delta_{nn'} E_n + I_{nn'}(r_q) + I_{nn'}(r_i) \]

where

\[ I_{nn'}(r_q) = \int \phi_{n q}(r_q) [A_q + \frac{1}{r_q}] \phi_{n'i}(r_q) d_{i q} \]

\[ (1-Z_q) \]

\[ \int \phi_{n q}(r_q) \left( \frac{1}{r_q} \right) \phi_{n'i}(r_q) d_{i q} \]

\[ r_q \]

\[ \phi_{n q}(r_q) \]

and \( A_q \) and \( r_q \) are the model potential parameters for the atom \( q \). \( F_{nn'}(r_i) \) represents integrals of the general form:

\[ I_{nn'} = \int \phi_{n q}(r_q) V_B \phi_{n'i}(r_A) d_{i A} \]

The evaluation of the integrals in equation 2.51 can be achieved by a transformation to elliptical co-ordinates and
closely follows the procedure outlined on pp 38-41. For the sake of completeness in this section we shall give a brief outline of the method for the case of s-functions. For this case,

\[
I_{nn'} = \frac{NN'}{4\pi} \sum_{s=0}^{n-1} \sum_{t=0}^{n'-1} \int_{B_{ns}} B_{n't} \left( \frac{z}{n} \right)^s \left( \frac{z'}{n'} \right)^t I_{st}
\]

where

\[
I_{st} = \int_0^\infty e^{-rA/n} v(r_B) r_A e^{-rA/n'} dr_A = (-1)^{s+t} \frac{\alpha^{s+t} I_\infty}{\alpha_n \alpha_{n'}}
\]

with,

\[
a_n = \frac{1}{n!} \quad \beta_n = \frac{1}{n!}
\]

Hence

\[
I = \int_0^\infty e^{-drA} v(r_B) dr_A
\]

This integral may be evaluated by a transformation to elliptical co-ordinates, assuming \( R > r^0 > \frac{R}{2} \).

\[
v(r_B) = A \quad ; \quad r_B < r^0
\]

\[
v(r_B) = -\frac{Z}{r_B} \quad ; \quad r_B > r^0
\]

then, \( \psi \)

\[
I = \frac{A\pi R^3}{4} \int_0^\infty \left[ \int_{v=-1}^{v=+1} \int_{u=-1}^{u=+1+x} w_{u+v} \left( 1 - v^2 \right) du \right] dv
\]
\[\begin{align*}
- \frac{2\pi R^2}{2} \int_{-x}^{v=x} \int_{u=v+1+x}^{u=\infty} e^{-a(u+v)(u+v)} \, du \, dv
&- \frac{2\pi R^2}{2} \int_{-x}^{-1} \int_{u=1}^{u=\infty} e^{-a(u+v)(u+v)} \, du \, dv

\text{where } \frac{2r^0}{R} = 1 + x = u \text{ and } a = \left( \frac{a_1}{n_1} + \beta_n \right) \frac{R}{2}

\text{from which,}
\end{align*}\]

\[\begin{align*}
I_\infty &= \frac{2\pi R^3}{8} \left[ C_2(a,u)A_0(2a) + 2C_1(a,u)A_1(2a) + A_2(a) - A_1(a) + \frac{(1 + x)^2}{4} C_1(a,u) - \frac{C_3(a,u)}{4} \\
&+ A_2(a)E_0(a) - A_0(a)E_2(a) - C_2(a,u)E_0(2a) - 2C_1(a,u)E_1(2a) \right] \\
&+ \frac{2\pi R^2}{2} \left[ \frac{1}{2} C_2(a,u) - (1 + x) C_1(a,u) \right] C_1(a,u)A_0(2a) - 2C_1(a,u)A_1(2a) \\
&- B_0(a)A_1(a) - A_0(a)B_1(a) - 2A_1(a)A_0(a) + A_2(a) - A_1(a) \\
&+ E_0(a)A_1(a) + E_1(a)A_0(a) - C_1(a,u)E_0(2a) - 2C_1(a,u)E_1(2a) \\
&+ C_1(a,u)A_0(a) - C_2(a,u)A_0(2a) - 2C_1(a,u)A_1(2a) \\
&- B_0(a)A_1(a) - A_0(a)B_1(a) - 2A_1(a)A_0(a) + A_2(a) - A_1(a) \\
&+ E_0(a)A_1(a) + E_1(a)A_0(a) - C_1(a,u)E_0(2a) - 2C_1(a,u)E_1(2a) \right] \\

\text{where}
\end{align*}\]

\[\begin{align*}
C_n(a,u) &= \int_u^n r^n e^{-ar} dr = \frac{e^{-au}}{a} \sum_{k=0}^{n} \frac{u^k}{k!} \\
&= \frac{e^{-au}}{a} \sum_{k=0}^{n} \frac{u^k}{k!} \\
A_n(a) &= \int_1^n r^n e^{-a} dr = C_n(a,1) \\
B_n(a) &= \int_{-1}^{-1} r^n e^{-a} dr = (-1)^{n+1} A_n(-a) - A_n(a) \\
E_n(a) &= \int_{-x}^{n} r^n e^{-ar} dr = \frac{e^{ax}}{a} \sum_{k=0}^{n} \frac{(-ax)^n}{(n-k)!} \\
&= \frac{e^{ax}}{a} \sum_{k=0}^{n} \frac{(-ax)^n}{(n-k)!} \end{align*}\]
A computer programme was written using these formulae for the calculation of s and p Rydberg series in linear triatomic molecules. Several of the integrals evaluated using equation \(2.59\) were checked using a 72-point Gaussian Quadrature programme.

(ii) Results and Discussion

In this discussion the computational aspects of the method outlined above will be emphasised and we shall postpone a detailed consideration of the relation of calculated Rydberg series to experimental data, e.g. vacuum u-v and electron impact spectra, to a later chapter.

The computer programme was written so that it could be applied to linear triatomic molecules in general, but it was used in particular for \(\text{CO}_2\), \(\text{CS}_2\), \(\text{CSe}_2\), \(\text{OCS}\) and \(\text{OCSe}\). Models s and p Rydberg series for these molecules were calculated to reproduce observed series converging to the lowest ionisation potential of the particular molecule.

In making these calculations a number of important factors had to be considered:

(a) The choice of expansion centre and the degree of i-spoiling for the Rydberg M.O.

(b) The effect of changing the point-charge distribution of the core.

These factors will be discussed for the two cases of symmetrical \(\text{XY}_2\) and unsymmetrical \(\text{XYZ}\) molecules.

Symmetrical \(\text{XY}_2\) molecules

(a) For symmetrical \(\text{XY}_2\) molecules it is necessary to expand
the Rydberg M.O. about the central atom Y to maintain the 
inversion symmetry inherent in the ground state nuclear 
conformation of these molecules and their ions. With a one-
centre expansion about the atom Y there are no matrix elements 
of the potential energy operator connecting s and p functions. 
The discussion on pp 51-55 suggests that there will be \( \sim 10\% \) 
s-d mixing in the lowest \( ns g \) terms of \( \text{CO}_2 \) and \( \sim 7\% \) p-f mixing 
in the lowest \( np u \) terms. These percentages will decrease in 
going to higher terms. Inclusion of these mixings in the 
calculation will cause small perturbations of levels calculated 
without including f-spoiling. Unfortunately d or f functions 
have not been included in the calculations presented in this 
thesis, although they could be incorporated in existing programmes. 
Since d and f functions are essentially non-penetrating the 
integrals involved could be evaluated by ignoring contributions 
from inside the ion-core.

(b) It was shown previously (p 44) that the quantum defect 
of a molecular Rydberg series, \( \mu_{\text{Mol}} \), can be divided into two 
parts \( \mu_{\text{pen}} + \mu_{\text{c.s.}} \). \( \mu_{\text{c.s.}} \) represents the contribution to the 
quantum defect arising from the non-spherical part of the 
potential and can be further subdivided into contributions 
from inside and outside the ion core:

\[
\mu_{\text{c.s.}} = \mu_{\text{c.s.}}^{\text{in}} + \mu_{\text{c.s.}}^{\text{out}}
\]

In the calculation \( \mu_{\text{c.s.}}^{\text{in}} \) is determined by the core
atomic model potential while $\nu_{\text{c.s.}}^{\text{out}}$ depends on the partial charge $\delta Z_i$ assigned to the atom $i$. (see p47). For Rydberg series converging to the lowest ionisation potential of a molecule,

\[ \sum_i \delta Z_i = 1, \]

but the individual $\delta Z_i$ must be determined from an effective point charge distribution assumed for the ion-core. For $YX_2$ molecules two extreme cases have been considered: Charge distribution A corresponding to a maximum separation of charge and distribution B corresponding to maximum delocalisation of charge

\[
\begin{align*}
+\frac{1}{2} & 0 +\frac{1}{2} & +\frac{1}{3} & +\frac{1}{3} & +\frac{1}{3} \\
X - Y - X & X - Y - X & & & \\
& & & & \\
& A & B & & & \\
\end{align*}
\]

The distributions appropriate to $CO_2$, $CS_2$ and $CSe_2$ should lie somewhere between these two extremes. $ns^q$, $np^u$ and $np^\pi$ Rydberg series were calculated for these molecules using $10s$ and $9p$ functions with charge distributions A and B. The results for $CO_2$ are given as an example in table 2.IV.

Table 2.IV shows that calculated term values are insensitive to changes in the charge distribution of the ion-core. $ns^q$ terms show the greatest dependence with a variation
Table 2.IV

Calculated Rydberg terms for CO₂

<table>
<thead>
<tr>
<th>n</th>
<th>CO₂ nsσ⁺</th>
<th>A (a.u.)</th>
<th>B (a.u.)</th>
<th>CO₂ npσ⁺</th>
<th>A (a.u.)</th>
<th>B (a.u.)</th>
<th>CO₂ npπ⁺</th>
<th>A (a.u.)</th>
<th>B (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>.11565</td>
<td>.11915</td>
<td>.09418</td>
<td>.09673</td>
<td>.09616</td>
<td>.09781</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>.05112</td>
<td>.05238</td>
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<td>.04399</td>
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<td>.04548</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
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<td>.02533</td>
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<td>.02622</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>.01902</td>
<td>.01623</td>
<td>.01651</td>
<td>.01704</td>
<td>.01704</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>.01300</td>
<td>.01326</td>
<td>.01147</td>
<td>.01163</td>
<td>.01196</td>
<td>.01195</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.00958</td>
<td>.00977</td>
<td>.00855</td>
<td>.00863</td>
<td>.00884</td>
<td>.00883</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of 4% of the lowest term value in going from distribution A to B; np^2_u terms show the least dependence.

This behaviour is very similar to that found for non-penetrating Rydberg M.O.'s. For these orbitals,

\[ \mu_{\text{Mol}} = \mu_{\text{pen}} + \mu_{\text{c.s.}}^{\text{in}} + \mu_{\text{c.s.}}^{\text{out}} = \mu_{\text{c.s.}} \]

The calculations of H. Hosoya\(^{32}\) show that for linear triatomics the dependence of the term value on the ion-core charge distribution is only a few percent of the term value and, for orbitals with the same \(n\) and \(l\) quantum numbers, smaller for \(\pi\) components than for \(\sigma\) components.

Non-symmetrical linear XYZ molecules

Linear XYZ molecules do not have the inversion symmetry of their symmetrical YX\(_2\) counterparts and it is no longer necessary to carry out the expansion of the Rydberg wavefunction about the central atom \(Y\). Indeed, one is at liberty to select any of the three atoms \(X\), \(Y\) or \(Z\) as the expansion centre for the wavefunction, and the effect of expanding about these different centres has been investigated.

\[ \int \phi_{s_d}(r_y) V_2 \phi_{p_c}(r_y) \, dr_y \]

are non-vanishing in contrast to their behaviour in symmetrical YX\(_2\) molecules. Calculations on OCS show that s-p mixing is
much larger than the expected s-d mixing in the lower s terms of CO₂. Inclusion of s-p mixing causes a mutual repulsion of the σ and π levels and can change term energies calculated without s-p mixing by as much as 15%. For this reason s-p mixing was included in all calculations of σ and π Rydberg series of linear XYZ molecules.

The effect of changing the expansion centre in OCS on calculated nsσ terms is shown in table 2.V. The nsσ series were calculated with charge distribution A. The table shows that changing the expansion centre in OCS affects the calculated nsσ term energies by ~3%. This figure represents the quality of one-centre expansions for XYZ molecules unless there are grounds for favouring an expansion about a particular atom in the molecule.

<table>
<thead>
<tr>
<th>Table 2.V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated nsσ Rydberg terms for OCS</td>
</tr>
<tr>
<td>Expansion Centre</td>
</tr>
<tr>
<td>n</td>
</tr>
<tr>
<td>----</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
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</tr>
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</tr>
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<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
</tbody>
</table>
For the case of XYZ molecules in which one atom, say atom X, has a much lower first ionisation potential than any of the other atoms in the molecule the expansion should be about the atom X. Examples of XYZ molecules of this type are SeCO and ICN where X is Se and I respectively. The energy levels of the atom X are so much lower than those of the atoms Y or Z, that the Rydberg Mo's of the XYZ molecule must be built up largely of X atom A.O's. Thus XYZ molecules of this kind have "localized" Rydberg Mo's centred on the atom X and a one-centre expansion about X should be a good approach to the calculation of the Rydberg series in these molecules.

E. Finn has studied the Rydberg series of OCSe and used the model potential approach presented in this thesis, with an expansion of the Mo's about the Se atom. nse, np and np+ series were calculated for this molecule and the agreement found with observed series in the vacuum u-v spectrum of OCSe demonstrates the usefulness of one-centre calculations for this type of molecule.

2.6 Two-centre expansions of CO₂ Rydberg wavefunctions

(i) Introduction

While the main body of work in this thesis employs one-centre expansions of molecular wavefunctions it is very instructive to attempt a many-centre expansion of wavefunctions to demonstrate its inappropriateness for the treatment
of Rydberg orbitals in triatomic molecules. Because of the large amount of work involved in extending one-centre calculations to many centres we have considered only s-functions on two centres; nevertheless the results clearly demonstrate the behaviour of separated atom wavefunctions in going along a Rydberg series and bring out the very important differences between $\sigma_{\ns}$ and $\sigma'_{\ns}$ orbitals.

(ii) Linear-dependence and two-centre expansions

The main weakness of the single-centre expansion technique is that it fails to take into account the singularities at the nuclei while often introducing a non-physical singularity at the arbitrarily chosen expansion centre. This deficiency may be overcome in principle by resorting to a multicentre expansion in which sets of functions are located at all of the nuclear positions. However, this approach must be used with great caution because approximate linear dependence is may arise which can cause serious problems in numerical computations. The two-centre calculations reported in this thesis employed linear combinations of hydrogen functions located at two nuclei in the molecule. The problem of near linear dependence was met with from the very beginning and its manifestations will now be discussed.

To ensure that linear dependence does not arise in a chosen basis set it is sufficient to orthonormalise all the functions of the set because non-degenerate orthogonal functions
are necessarily linearly independent. A non-orthogonal basis set \( \{ \chi_n \} \) may be converted to an orthonormal set \( \{ \phi_n \} \) by means of a matrix transformation \( A \):

\[
\phi_{\mu} = \sum_{\nu} \chi_{\nu} A_{\mu \nu} \quad 2.61
\]

with

\[
\int \chi_{\mu} \chi_{\nu} d\tau = S_{\mu \nu} ; \quad \int \phi_{\mu} \phi_{\nu} d\tau = \delta_{\mu \nu} \quad 2.62
\]

The non-orthogonality of the set \( \{ \chi_n \} \) is manifest in the non-zero overlap integrals \( S_{\mu \nu} \).

P.O. Löwdin\(^4\) has shown that the general solution of the orthonormality problem has the form

\[
\phi = \chi S^{-\frac{1}{2}} \quad 2.63
\]

where \( S^{-\frac{1}{2}} \) is the reciprocal square root of the overlap matrix. \( S^{-\frac{1}{2}} \) may be determined by finding the unitary transformation, \( U \), which diagonalises \( S \). If \( U \) is the matrix formed from the eigenvectors of \( S \) then,

\[
SU = U[\lambda_i \delta_{ij}] \quad 2.64
\]

where the \( \lambda_i \) are the eigenvalues of the matrix \( S \) and

\[
S_{ik} = \sum_{j} U_{ij} \lambda_{ij}^{-\frac{1}{2}} U_{kj} \quad 2.65
\]

The importance of the overlap matrix in showing the presence of linear dependence or near linear dependence in
a basis set \( \{ \chi_n \} \) is now apparent. Thus pre-multiplying equation 2.64 by \( U^+ \) gives

\[
U^+ S U = \text{diag} \left( \lambda_1, \lambda_2, \ldots \right)
\]

because \( U^+ U = 1 \)

A relation,

\[
U^+ S U = 0
\]

necessarily implies

\[
\chi U = 0
\]

i.e. a linear dependency. Similarly the minimum value of \( U^+ S U \) is a measure of the linear dependence of the set \( \{ \chi_n \} \).

To investigate the possibility of linear dependence in a two-centre calculation of the Rydberg series in CO\(_2\) the overlap matrix must be determined. The non-orthogonal basis set \( \{ \chi_n \} \) was composed of sub-sets \( \chi_{An}, \chi_{Bn} \) of hydrogen functions separated by a distance \( R \), and overlap integrals were evaluated using the transformation to elliptical co-ordinates given on p.40. Computer programmes were written for the evaluation of overlaps at any internuclear separation, \( R \), for the following cases:

\[
S(ns, n's) \quad n',n = 1, 2, \ldots 10
\]

\[
S(np, n'p) \quad n',n = 2, 3, \ldots 10
\]

Because equilibrium \( R \) values in most molecules are in the range 2-4 \text{ a.u.}'s computed overlaps, when \( n=n' \), are given in table 2.VI at \( R=2.0 \) and \( R=4.0 \) \text{ a.u.}'s.

Table 2.VI shows that in going to higher \( n \) the overlap rapidly obtains a value close to \( 1 \); at the same time the limit of exact linear dependence is being approached.
**Table 2.VI**

Overlap Integrals for Hydrogen Functions at R=2.0 and R=4.0 a.u.

<table>
<thead>
<tr>
<th>n</th>
<th>R=2.0</th>
<th>R=4.0</th>
<th>R=2.0</th>
<th>R=4.0</th>
<th>R=2.0</th>
<th>R=4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5865</td>
<td>0.1893</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.8829</td>
<td>0.7308</td>
<td>-0.7358</td>
<td>-0.8256</td>
<td>0.9074</td>
<td>0.6947</td>
</tr>
<tr>
<td>3</td>
<td>0.9426</td>
<td>0.8424</td>
<td>-0.8819</td>
<td>-0.6484</td>
<td>0.9537</td>
<td>0.8627</td>
</tr>
<tr>
<td>4</td>
<td>0.9658</td>
<td>0.8971</td>
<td>-0.9324</td>
<td>-0.7893</td>
<td>0.9765</td>
<td>0.9198</td>
</tr>
<tr>
<td>5</td>
<td>0.9773</td>
<td>0.9277</td>
<td>-0.9561</td>
<td>-0.8578</td>
<td>0.9849</td>
<td>0.9470</td>
</tr>
<tr>
<td>6</td>
<td>0.9838</td>
<td>0.9466</td>
<td>-0.9672</td>
<td>-0.8971</td>
<td>0.9894</td>
<td>0.9623</td>
</tr>
<tr>
<td>7</td>
<td>0.9879</td>
<td>0.9589</td>
<td>-0.9771</td>
<td>-0.9220</td>
<td>0.9922</td>
<td>0.9718</td>
</tr>
<tr>
<td>8</td>
<td>0.9906</td>
<td>0.9675</td>
<td>-0.9824</td>
<td>-0.9338</td>
<td>0.9940</td>
<td>0.9780</td>
</tr>
<tr>
<td>9</td>
<td>0.9925</td>
<td>0.9736</td>
<td>-0.9860</td>
<td>-0.9506</td>
<td>0.9952</td>
<td>0.9824</td>
</tr>
<tr>
<td>10</td>
<td>0.9939</td>
<td>0.9781</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.VII**

Smallest Eigenvalues for 8 Hydrogen s-functions at R=2.0 and R=4.0 a.u.

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.99330</td>
<td>0.32362</td>
<td>0.12325</td>
<td>0.035640</td>
<td>0.02733</td>
<td>0.012749</td>
<td>0.00502</td>
<td>0.00117</td>
</tr>
<tr>
<td>3.0</td>
<td>0.53477</td>
<td>0.08992</td>
<td>0.03201</td>
<td>0.01433</td>
<td>0.00690</td>
<td>0.00320</td>
<td>0.00126</td>
<td>0.00029</td>
</tr>
</tbody>
</table>
To determine values of,

\[ \lambda_{\text{min}} = \min(U^+SU), \]

the overlap matrix for 10 s-functions on each centre was obtained and diagonalized using the computer library subroutine EA01B. This subroutine employs the Householder method 50 in which the matrix is reduced to a tri-diagonal form by means of similarity transformations. Unfortunately unacceptable eigenvalues were obtained as the result of the accumulation of rounding errors. This comes about because the overlap matrix, S, has large off-diagonal elements and converges to a form with vanishing eigenvalues; a matrix of this type is ill-conditioned for the iterative process needed for diagonalization. Here we observe a manifestation of near linear dependence which sets a limit on the maximum dimension of S and consequently on the size of the basis set used in the two centre calculations.

EA01B successfully diagonalized the overlap matrix for 8 Hydrogen s-functions on each centre at R=2.0 and R=4.0 a.u. and gave the eight smallest eigenvalues \( \lambda_n \) shown in table 2.7. However, with this 16-function basis set (8 on each centre) rounding errors were still troublesome in the evaluation of certain two-centre integrals, even when double precision arithmetic was employed; these manifestations of near linear dependence were eliminated from the programme when the basis set was restricted to a maximum of 14 functions (7 on each centre). This indicates that, for this type of two-centre calculation, \( \lambda_n \) should be >0.001 if computational problems
due to near linear dependence are to be avoided.

The overlap matrix, $S$, is not only important in checking for linear dependence in a non-orthogonal basis-set but can also be used to determine the roots of the determinantal equation arising from variational solutions of Schrödinger's equation,

$$H\Psi_i = E_i \Psi_i$$ \hspace{1cm} 2.69

The M.O's $\Psi_i$ are formed from linear combinations of the non-orthogonal set $\{\chi_n\}$,

\[ \Psi_i = \sum_{\mu=1}^{N} \chi_\mu c_{\mu i} \]

or in matrix notation,

$$\Psi = \chi C$$ \hspace{1cm} 2.70

The expansion coefficients, $c_{\mu i}$, are obtained by the application of variational theory leading to the secular equations,

$$H C = E S C$$ \hspace{1cm} 2.71

Computing the roots of the determinantal equation,

$$|H - SE| = 0$$ \hspace{1cm} 2.72

involves much more effort than the case in which $S$ is the unit matrix, but the former can be reduced to the latter if the matrix $H$ is replaced by,

$$H' = S^{-\frac{1}{2}} H S^{-\frac{1}{2}}$$ \hspace{1cm} 2.73
and the substitution,
\[ C' = \frac{1}{s} c \]
as made in 2.70.

Equation 2.71 now becomes,
\[ H'C' = C' E \]

This transformation is equivalent to expressing the original operator \( H \) as a matrix with the new orthogonal basis \( \{ \phi_n \} \), since from equations 2.70 and 2.74,
\[ \psi = \chi C = \chi S^{-\frac{1}{2}} C' = \phi C' \]

A computer programme was written to calculate s Rydberg series in linear \( YX_2 \) molecules using an expansion of hydrogen functions about the two \( X \) atoms. It was necessary to evaluate three centre integrals of the type:
\[ V_{nn'} = \int \chi_n(\mathbf{r}_A) \chi_n(\mathbf{r}_B) \chi_{n'}(\mathbf{r}_C) \, d\tau = \langle a| V_C |b \rangle \]

Although these can be evaluated exactly it was more convenient to use the well-known Mulliken approximation in these initial studies:
\[ \langle a| V_C |b \rangle = \frac{1}{2} S_{ab} \left( \langle a| V_C |a \rangle + \langle b| V_C |b \rangle \right) \]

(iii): Results and Discussion

With 7 s-functions located on each of the two oxygen atoms in \( CO_2 \) two Rydberg series should be obtained from the calculation corresponding to in-phase and out-of-phase overlap.
of the functions. These series may be given the usual separated
atom designations, \( g_{ns} \) and \( u_{ns} \). R.S. Mulliken\(^{10}\) has shown
that the forms \( g_{ns} \) and \( u_{ns} \) correlate at small \( R \) with the
united-atom Mo's \( n \sigma_g \) and \((n+1)p \sigma_u \) respectively.

The one-centre (united-atom) and two-centre (separated
atoms) calculations presented in this thesis represent different
approximations to the same Rydberg Mo's, and should presumably
give similar series of Rydberg terms.

Table 2.VIII gives a comparison of calculated one-centre
and two-centre \( \sigma_g \) and \( \sigma_u \) term energies for \( \text{CO}_2 \).

<table>
<thead>
<tr>
<th></th>
<th>( n \sigma_g )</th>
<th>( g_{ns} )</th>
<th>( n \sigma_u )</th>
<th>( u_{(n-1)s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1157</td>
<td>0.1089</td>
<td>0.0942</td>
<td>-0.0313</td>
</tr>
<tr>
<td>3</td>
<td>0.0511</td>
<td>0.0567</td>
<td>0.0429</td>
<td>-0.0913</td>
</tr>
<tr>
<td>4</td>
<td>0.0290</td>
<td>0.0351</td>
<td>0.0248</td>
<td>-0.1140</td>
</tr>
<tr>
<td>5</td>
<td>0.0186</td>
<td>0.0236</td>
<td>0.0162</td>
<td>-0.1305</td>
</tr>
</tbody>
</table>

Inspection of the table shows that for the \( \sigma_g \) series
the two-centre term values are in reasonable agreement with the
one-centre terms, but the \( u_{ns} \) terms bear no resemblance to
the one-centre \( \sigma_u \) terms. Indeed the negative sign in front
of the calculated \( u_{ns} \) terms means the states are unbound
and lie above the ionisation limit.
In order to see why the one-centre and two-centre calculations approximately agree for $\sigma_g$ levels but totally disagree for $\sigma_u$ levels it is necessary to investigate the behaviour of the two-centre functions close to the united-atom limit.

The two-centre Rydberg Mo's are built from linear combinations of hydrogen s-functions $\chi_{\mu}$:

$$\psi_i = \sum_{\mu=1}^{N} \chi_{\mu} c_{\mu i}$$  \hspace{1cm} 2.79

where the set $\{\chi_{\mu}\}$ is composed of $N/2$ functions $\chi_{AN}$ on centre A and $N/2$ functions $\chi_{BN}$ on B.

Because,

$$\left(\chi_{AV} + C_{V1}^2 \chi_{A1} + C_{V2}^2 \chi_{A2} + \ldots\right) + \left(\chi_{BV} + C_{V1}^2 \chi_{B1} + C_{V2}^2 \chi_{B2} + \ldots\right)$$

$$= \left(\chi_{AV} - \chi_{BV}\right) + C_{V1}^2 \left(\chi_{A1} - \chi_{B1}\right) + C_{V2}^2 \left(\chi_{A2} - \chi_{B2}\right) + \ldots$$

symmetrized, the Mo's are:

$$\psi_i (\sigma_g) = \sum_{V=1}^{N/2} \left(\chi_{AV} + \chi_{BV}\right) c_{VI}$$  \hspace{1cm} 2.80

$$\psi_i (\sigma_u) = \sum_{V=1}^{N/2} \left(\chi_{AV} - \chi_{BV}\right) c_{VI}$$  \hspace{1cm} 2.81

Very close to the united-atom limit $\psi_i (\sigma_g)$ consists of LCAO forms of the type,

$$\psi_g = \frac{1}{\sqrt{2 + 25n}} \left(\chi_{An} + \chi_{Bn}\right)$$  \hspace{1cm} 2.82

and these will be almost identical to the united-atom functions $C_n$ where $C$ is the mid-point of A and B. Hence the one-centre
and two-centre calculations should give similar results in this case.

\[ \psi_i(\sigma_u) \text{ contains LCAO forms of the type,} \]

\[ \psi_u = \frac{1}{\sqrt{2-2s_n}} \{ \chi_{An} - \chi_{Bn} \} \]

and close to the united-atom limit \( \{ \chi_{An} - \chi_{Bn} \} \) becomes zero and the normalising factor \( \frac{1}{\sqrt{2-2s}} \) becomes infinite. The form \( \psi_u \) in the limit can be obtained by applying the theory of indeterminant forms. With the \( z \)-axis joining \( A \) to \( B \),

\[ \lim_{z \to 0} \frac{d\psi_u}{dz} \]

which is, not a united-atom wavefunction. Correlation diagrams show that the correct anti-symmetric combination of two \( s \) levels at the united-atom limit must be a \( p \) level, and \( \psi_u \) must be given some \( p \) character to allow for this. The inclusion of \( p \) functions in the basis set is necessary because of "forced s-p hybridization" - a term used to describe the consequences of the fact that an \( s \)-orbital on one centre is non-orthogonal to a \( p \)-orbital on another centre. Thus the correct forms for \( \sigma_{qs} \) and \( \sigma_{us} \) must be:

\[ \psi(\sigma_{qs}) = N \left\{ \sum_{n=1}^{\infty} c_n (ns_A + ns_B) + \sum_{m=1}^{\infty} c_m (mp_A + mp_B) \right\} \]

\[ \psi(\sigma_{us}) = N \left\{ \sum_{n=1}^{\infty} c_n (n'p_A + n'p_B) + \sum_{m=1}^{\infty} c_m (ms_A - ms_B) \right\} \]

Close to the united-atom the \( C_m \to 0 \), \( \psi(\sigma_{qs}) \) becomes equivalent to \( \psi_i(\sigma) \) in 2.80, but \( \psi(\sigma_{us}) \) does not become equivalent to \( \psi_i(\sigma_u) \) in 2.81.

The fact that the calculated energies for the two-centre \( \sigma \) MO's using only \( s \)-functions, are similar to the one-centre \( \sigma \) energies shows that the \( c_m \) in 2.85 must indeed be small and
\( \Phi(\sigma_{u}ns) \) is close to a united-atom ns\( \sigma_{g} \) function. On the other hand, the calculated energies of two-centre \( \sigma_{u} \) Mo's derived from s-functions must be seriously in error because \( \Phi_{i}(\sigma_{u}) \) cannot even approximately represent a united-atom np\( \sigma_{u} \) function. The out-of-phase overlap of s-functions in \( \Phi_{i}(\sigma_{u}) \) forms very unstable states which become unbound close to the united-atom limit; the inclusion of p-functions in \( \Phi(\sigma_{u}ns) \) stabilizes the M.O. by allowing electron density to move out of regions of unfavourable overlap. (See Fig. 2.5).
Fig. 2.V

The Effect of Including p Functions in Two-centre $\sigma_{u ns}$ MO's

\[ E \]

\[ R \]

\[ J_{u ns} = N(ns_A - ns_B) \]

\[ \sigma_{u ns} = N(a(ns_A - ns_B) + b(np_A + np_B)) \]
CHAPTER 3
RYDBERG TRANSITIONS IN CO$_2$

3.1 Coupling Schemes for the Rydberg States of CO$_2$

(i) Introduction

The basic problem studied in this thesis is the interpretation of Rydberg series observed in the absorption spectra of certain linear triatomic molecules. Rydberg absorption spectra arise when a molecule in its ground electronic state undergoes a transition to an excited state, and a clear understanding of these transitions requires a knowledge of both the ground and excited states of the molecule.

A molecular state is specified to a first approximation by an electron configuration in which each of the electrons in the molecule is assigned a one-electron function or orbital. These orbitals are eigenfunctions of a first order Hamiltonian $H_0$ which ignores electron correlation and contains only one-electron operators.

Ground state MO configurations can be obtained from LCAO-MO-SCF calculations. The first MO calculation on the ground state of CO$_2$ was carried out by J.F. Mulligan in 1951 and since then the calculations have been repeated, with improvements, by several authors. These calculations indicate that the ground state configuration of CO$_2$ is:

$\{1\sigma_g\}^2 \{1\sigma_u\}^2 \{2\sigma_g\}^2 \{3\sigma_g\}^2 \{2\sigma_u\}^2 \{4\sigma_g\}^2 \{3\sigma_u\}^2 \{1\pi_u\}^4 \{1\pi_g\}^4$.

Although the ordering of some of the inner MO's depends on
the basis set used in the calculation.

The most important feature of this configuration is the form of the highest occupied \( l\pi_g \) M.O. This M.O. is essentially non-bonding and is mainly composed of two oxygen 2p A.O.'s. This conclusion is confirmed by the observation that removal of an electron from \( \text{CO}_2 \) to form \( \text{CO}_2^+ \) in its ground state is accompanied by a very small change in the bond length \((1.1621 \text{ Å} + 1.1770 \text{ Å})^{54}\).

Rydberg states of \( \text{CO}_2 \) with excitation energies less than the lowest ionisation potential of the molecule, \( I.P.\text{CO}_2 \), are formed by the promotion of a \( l\pi_g \) electron to a united-atom orbital designated by the quantum numbers \( n\lambda \) with \( n \geq 3 \) and \( n \geq i+1 \).

The single-centre model potential calculations presented in the first half of this thesis determine the ionisation potential, \( I.P.\text{Ryd} \), of an electron in one of these united-atom Rydberg orbitals, and the approximate form of the orbital. If the lowest ionisation potential of \( \text{CO}_2 \) is known the excitation energy, \( \Delta E \), for the transition,

\[
\ldots(l\pi_g)^3 n\lambda \text{ or } u \ldots(l\pi_q)^4
\]

may be calculated because \( \Delta E = I.P.\text{CO}_2 - I.P.\text{Ryd} \).

The Rydberg transition indicated by 3.1 does not necessarily represent a single transition in the \( \text{CO}_2 \) absorption spectrum because a configuration is obtained from an approximate Hamiltonian, \( H^e \), and does not fully specify the state of the system. A complete specification can be obtained from a
Hamiltonian, $H^e$, which includes the electron interaction term, $\frac{1}{r_{ij}}$. This term introduces couplings between spin and orbital motions of the electrons.

The effects of using the approximate Hamiltonian $H^e$ are apparent for configurations involving open-shells because spin-functions can be added to these orbital configurations in many different ways. In this case several wavefunctions may belong to a single orbital configuration and represent states which are degenerate with respect to $H^e$. This degeneracy is resolved by the complete electrostatic Hamiltonian, $H^e$, giving states with slightly different energies.

The form of the eigenfunctions of $H^e$ can be obtained from a consideration of the coupling of the various spin and orbital angular momenta in the molecule, and from this the number and symmetry properties of states belonging to the same electron configuration can be determined.

(ii) The \((\pi^o)\hat{3}\) configuration of the ion CO$_2^+$

The coupling in the \((\pi^o)\hat{3}\) core of CO$_2^+$ is designated \((\lambda, S)\), the molecular-analogue of the well known Russell-Saunders or \((L, S)\) coupling applicable to light atoms. In \((\lambda, S)\) coupling it is assumed that the spin-spin and orbit-orbit interactions are much larger than spin-orbit interactions.

The individual components, $M_\lambda$, of the orbital angular momenta along the molecular axis couple to form a resultant $M_L$ and the energy of orientation depends on $|M_L| = \lambda$. 
The individual spins, $s_i$, from a resultant $S$ and the component of $S$ along the molecular axis is called $\Sigma$. $\Sigma$ is taken as positive when it has the same sign as $M_L$ and negative when it has the opposite sign.

The multiplet splitting due to the magnetic interaction of $\Lambda$ and $\Sigma$ is given to first order by,

$$ T = T_0 + \tilde{A} \Lambda \Sigma $$ \hspace{1cm} \text{(3.2)}

where $\tilde{A}$ is called the spin-orbit coupling constant, and the energy of a multiplet component is specified by the total angular momentum along the molecular axis:

$$ \Omega = |\Lambda + \Sigma| = |M| $$ \hspace{1cm} \text{(3.3)}

For the $\ldots (\pi_g)^3$ configuration of $\text{CO}_2^+$, $\Lambda=1$ and $S=\frac{1}{2}$.

Possible determinantal wavefunctions, $\phi(M_L, \Sigma)$ are:

$$ \phi (1, \frac{1}{2}^+) = \frac{1}{\sqrt{4!}} |\pi g(1)\alpha(1)\pi g(2)\beta(2)\pi g(3)\alpha(3)| $$

$$ \phi (1, \frac{1}{2}^-) = \frac{1}{\sqrt{4!}} |\pi g(1)\alpha(1)\pi g(2)\beta(2)\pi g(3)\alpha(3)| $$

$$ \phi (1, \frac{1}{2}^+) = \frac{1}{\sqrt{4!}} |\pi g(1)\alpha(1)\pi g(2)\beta(2)\pi g(3)\beta(3)| $$

$$ \phi (1, \frac{1}{2}^-) = \frac{1}{\sqrt{4!}} |\pi g(1)\alpha(1)\pi g(2)\beta(2)\pi g(3)\beta(3)| $$

Two states may be constructed from these wavefunctions:

(written using an abbreviated notation for the determinants)
The spin-orbit coupling constant, $\lambda$, for CO$_2^+$ is 159.5 cm$^{-1}$.

(iii) The $(\pi_g)^3\sigma_u$ or $\pi$ configuration of CO$_2$

In highly excited Rydberg states of CO$_2$, derived from the $(\pi_g)^3\sigma_u$ or $\pi$ configuration, the Rydberg electron is subject to a very small $\frac{1}{r_{ij}}$ interaction and is coupled to the core by the coulomb field of the combined system of nuclei and core electrons. The total angular momentum of the Rydberg electron, $\omega$, is coupled to the molecular axis via the total angular momentum of the core, $\Omega_C$. This situation is referred to as $(\Omega_C, \omega)$ coupling.

Wavefunctions, $\psi_o(\Omega_C, \omega, n)$ for $(\Omega_C, \omega)$ coupled states of CO$_2$ in the $(\pi_g)^3\sigma_u$ or $\pi$ configuration are:

$$\psi_o(\frac{1}{2}, \frac{1}{2}, -1) = \frac{(1)}{\sqrt{2.41}} \begin{pmatrix} |a88a| + |a888| \end{pmatrix}$$

$$\psi_o(\frac{1}{2}, \frac{1}{2}, 0^+) = \frac{(1)}{\sqrt{2.41}} \begin{pmatrix} |a888| + |a88a| \end{pmatrix}$$

$$\psi_o(\frac{3}{2}, \frac{1}{2}, 1) = \frac{(1)}{\sqrt{2.41}} \begin{pmatrix} |a8a8| + |a88a| \end{pmatrix}$$

$$\psi_o(\frac{3}{2}, \frac{1}{2}, 2) = \frac{(1)}{\sqrt{2.41}} \begin{pmatrix} |a88a| + |a888| \end{pmatrix}$$
If the σ electron is in a low lying Rydberg orbital the \( \frac{1}{r_{ij}} \) interaction of the Rydberg electron with the core electrons is comparable to the average \( \frac{1}{r_{ij}} \) interaction between the core electrons, and the \((\pi_{g})^{3}\sigma_{u}\) or \(\sigma_{g}\) configuration will exhibit \((\Lambda, S)\) coupling.

Wavefunctions \(\psi_{o}(^{2S+1}\Lambda_{\Pi})\) for \((\Lambda, S)\) coupled states of \(\text{CO}_{2}\) in the \((\pi_{g})^{3}\sigma_{u}\) or \(\sigma_{g}\) configuration are:

\[
\psi_{o}(^{1}\Pi_{1}) = \frac{1}{\sqrt{A_{1}}} \left( |a\bar{a}\bar{a}| + |a\bar{a}\bar{a}| - \{|a\bar{a}\bar{a}| + |a\bar{a}\bar{a}|\} \right)
\]

\[
\psi_{o}(^{3}\Pi_{1}) = \frac{1}{\sqrt{A_{1}}} \left( |a\bar{a}\bar{a}| + |a\bar{a}\bar{a}| \right)
\]

\[
\psi_{o}(^{3}\Pi_{2}) = \frac{1}{\sqrt{A_{1}}} \left( |a\bar{a}\bar{a}| + |a\bar{a}\bar{a}| \right)
\]

A diagram showing the correlation of states derived from a \((\pi_{g})^{3}\sigma_{u}\) configuration in ideal \((\Lambda, S)\) and ideal \((\Omega, \omega)\) coupling can be constructed using the following considerations.

(i) The wavefunctions for the \(\Omega=0\) and \(\Omega=2\) states are the same in \((\Lambda, S)\) and \((\Omega, \omega)\) coupling. The wavefunctions and energy levels for these states remain unchanged throughout intermediate coupling ranges.

(ii) The two \(\Omega=1\) states mix in coupling intermediate between \((\Lambda, S)\) and \((\Omega, \omega)\). Starting from the \((\Lambda, S)\) states \(^{3}\Pi_{1}\) and \(^{1}\Pi_{1}\),
new wavefunctions for intermediate coupling are:

\[ \psi_1(3\Pi) = N \{ \alpha \psi_0(3\Pi_1) + \beta \psi_0(1\Pi_1) \} \]

\[ \psi_1(1\Pi) = N \{ \gamma \psi_0(3\Pi_1) + \delta \psi_0(1\Pi_1) \} \]

Comparison with the \( (\Sigma, \omega) \) coupled states \( \psi_0(\frac{1}{2}, \frac{1}{2}, 1) \) and \( \psi_0(\frac{3}{2}, \frac{1}{2}, 1) \) shows that for ideal \( (\Gamma, \omega) \) coupling \( \psi_1(3\Pi) \) and \( \psi_1(1\Pi) \) consist of equal mixtures of \( \psi_0(3\Pi_1) \) and \( \psi_0(1\Pi_1) \). (i.e. \( \alpha = \beta = 1 \) and \( \gamma = 1, \delta = -1 \)).

The correlation diagram (Fig. 3.1) shows that the type of coupling applicable to the Rydberg states of \( \text{CO}_2 \) derived from the \( \left( \pi_g \right)^3 \sigma_u \) configuration depends on the ratio of the singlet-triplet splitting in the Rydberg state, \( X \), to the spin-orbit coupling in the ion core \( \Lambda \).

The correlation diagram is also valid for the \( \left( \pi_g \right)^3 \sigma_u \) configuration of \( \text{CS}_2 \) and \( \text{CSe}_2 \) except that case (C) effects must be taken into account because of the larger spin-orbit coupling in these molecules.

In Hund's case (a) the multiplet splittings are given by equation 3.2. The molecular electric field is so strong that \( \mathbf{I} \) precesses rapidly around the figure axis and the vector component of \( \mathbf{I} \) perpendicular to the axis averages to zero. In Hund's case (c) the atomic \( \mathbf{I} \) and \( \mathbf{S} \) couplings are strong compared to the effects of the departure of the molecule from atomic conditions and the magnetic interaction of the perpendicular components of \( \mathbf{I} \) and \( \mathbf{S} \) causes the different multiplet
Fig. 3.1

Correlation of States Between Ideal ($\sigma$,S) and Ideal ($\sigma',\omega$) Coupling for a $(-q)^{3}\sigma_u$ Configuration
components to depart from the spacings given by equation 3.2. The degeneracies associated with states having \( \lambda = - \frac{1}{2} \) if \( \lambda = 0 \) are removed so that \( \Omega = 0 \) states are split into two components classified \( 0^+ \) or \( 0^- \) according as the wavefunction is even or odd as regards reflection of orbital and spin co-ordinates together in any plane containing the nuclei.

(iv) The \( \sum \Pi \Pi \Pi \) \( \pi_u \) configuration of \( \text{CO}_2^- \).

The \( \Pi \Pi \Pi \) \( \pi_u \) configuration of \( \text{CO}_2 \) in \( \Pi \Pi \Pi \) coupling has \( \Omega = \frac{1}{2} \) or \( \frac{3}{2} \) for the \( \pi_u \) Rydberg electron and \( \Omega = \frac{1}{2} \) or \( \frac{3}{2} \) for the \( \Pi \Pi \Pi \) core. The spin-orbit coupling constant \( \lambda \) of the \( \pi_u \) electron is very much smaller than the spin-orbit coupling constant \( \lambda \) of the core and \( \Delta = 0 \) as the Rydberg electron moves to higher orbitals.

The state wavefunctions, \( \psi \left( \Pi \Pi \Pi, \Omega \right) \) for the \( \Pi \Pi \Pi \) \( \pi_u \) configuration of \( \text{CO}_2 \) in \( \Pi \Pi \Pi \) coupling are:

\[
\begin{align*}
\psi \left( \frac{1}{2}, \frac{3}{2}, 2 \right) &= \frac{1}{\sqrt{2 \cdot 4!}} \left( |a^2a| + |a^3a^2| \right) \\
\psi \left( \frac{1}{2}, \frac{3}{2}, 1 \right) &= \frac{1}{\sqrt{2 \cdot 4!}} \left( |a^3a^2a| + |a^2a^2a| \right) \\
\psi \left( \frac{1}{2}, \frac{1}{2}, 0 \right) &= \frac{1}{\sqrt{2 \cdot 4!}} \left( |a^2a^2| + |a^3a^2| \right) \\
\psi \left( \frac{1}{2}, \frac{1}{2}, 1 \right) &= \frac{1}{\sqrt{2 \cdot 4!}} \left( |a^3a^2| + |a^2a^3| \right) \\
\psi \left( \frac{3}{2}, \frac{3}{2}, 0 \right) &= \frac{1}{\sqrt{2 \cdot 4!}} \left( |a^2a^2| + |a^3a^2| \right) \\
\psi \left( \frac{3}{2}, \frac{3}{2}, 3 \right) &= \frac{1}{\sqrt{2 \cdot 4!}} \left( |a^3a^2| + |a^2a^3| \right)
\end{align*}
\]
\[ \psi_0 \left( \frac{3}{2}, \frac{1}{2}, 2 \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a\bar{a}| + |a\bar{a}a\bar{a}| \right] \]

\[ \psi_0 \left( \frac{3}{2}, \frac{1}{2}, 1 \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

The \( (\pi g)^3 \pi_u \) configuration in \((\Delta, S)\) coupling has \( \Delta = 0 \) or 2 and \( S = 1 \) or 0, giving \( 1,3_\Delta \) and \( 1,3_\Lambda \) states. In a strong electric field with \( M_L = 0 \) there is no magnetic field to orient the spin \( S \) so that \( M_S \) and \( \Sigma \) are not defined for \( \Sigma \) states. However for singlet \( \Sigma \) levels a virtual \( \Sigma \) value of 0 can be assigned. For triplet \( \Sigma \) levels the zero coupling of \( S \) to the internuclear axis is referred to as Hund's case (b). Tendencies towards Hund's case (c) when the magnetic interactions are large, cause \( 3_\Sigma^+ \) states to split into \( 0^- \) and \( 1^- \) states while \( 3^- \) states give \( 0^+ \) and \( 1^+ \) states.

The state wavefunctions, \( \psi_0 \left( ^{2g+1} \Lambda_u \right) \), for the \((\pi g)^3 \pi_u \) configurations of \( \text{CO}_2 \) in \((\Delta, S)\) coupling are:

\[ \psi_0 \left( ^3 \frac{1}{2}_\Sigma \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a\bar{a}| + |a\bar{a}a\bar{a}| \right] \]

\[ \psi_0 \left( ^3 \frac{3}{2}_\Sigma \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| + |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^3 \frac{1}{2}_\Pi \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^1 \frac{1}{2}_\Pi \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^1 \frac{3}{2}_\Pi \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^1 \frac{1}{2}_\Delta \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^1 \frac{3}{2}_\Delta \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^1 \frac{1}{2}_\Lambda \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]

\[ \psi_0 \left( ^1 \frac{3}{2}_\Lambda \right) = \frac{1}{\sqrt{2} \sqrt{4!}} \left[ |a\bar{a}a| + |a\bar{a}a| \right] \]
\[ \phi_0 (^3\Sigma_{0}^-) = \frac{1}{\sqrt{4/4}} [^+_+_+_+ |a\beta\alpha\alpha| + ^+_+_+_+ |a\beta\alpha\beta| + ^+_+_+_+ |a\beta\alpha\beta| + ^+_+_+_+ |a\beta\beta\alpha|] \]

\[ \phi_0 (^3\Sigma_{0}^+) = \frac{1}{\sqrt{4/4}} [^+_+_+_+ |a\beta\alpha\alpha| - ^+_+_+_+ |a\beta\alpha\beta| + ^+_+_+_+ |a\beta\beta\alpha| - ^+_+_+_+ |a\beta\beta\alpha|] \]

\[ \phi_0 (^3\Sigma_{1}^-) = \frac{1}{\sqrt{2/4}} [^+_+_+_+ |a\beta\alpha\beta\alpha| + ^+_+_+_+ |a\beta\alpha\beta\alpha| + ^+_+_+_+ |a\beta\beta\alpha\alpha| + ^+_+_+_+ |a\beta\beta\alpha\alpha|] \]

\[ \phi_0 (^3\Sigma_{1}^+) = \frac{1}{\sqrt{2/4}} [^+_+_+_+ |a\alpha\alpha\beta\alpha| - ^+_+_+_+ |a\alpha\alpha\beta\alpha| - ^+_+_+_+ |a\alpha\beta\alpha\alpha| + ^+_+_+_+ |a\alpha\beta\alpha\alpha|] \]

A diagram showing the correlation of states derived from the \( ^3 \Sigma_u \) of CO₂ in (\( \Lambda, S \)) and (\( \Omega_C, \omega \)) coupling can be constructed using the following considerations:

**States**

There is only one state whose \( \Lambda \) value occurs only once, this is \( ^3 \Lambda_{3/2} \) in (\( \Lambda, S \)) coupling and \( \left( ^3 \Lambda_{3/2} \right)_3 \) in (\( \Omega_C, \omega \)) coupling. The state wavefunctions are the same in either coupling scheme and remain unchanged throughout intermediate coupling ranges.

There are two \( \Omega=2 \) states corresponding to \( ^3 \Lambda_{1/2} \) and \( ^1 \Lambda_{1/2} \) in (\( \Lambda, S \)) coupling and \( \left( ^3 \Lambda_{1/2} \right)_2 \) and \( \left( ^3 \Lambda_{1/2} \right)_2 \) in (\( \Omega_C, \omega \)) coupling. The (\( \Lambda, S \)) wavefunctions for these states will become increasingly mixed in going over to (\( \Omega_C, \omega \)) coupling.

The \( ^3 \Lambda_{1} \) wavefunction is the same as the (\( \Omega_C, \omega \)) wavefunction for \( \left( ^1 \Lambda_{1/2} \right)_1 \). In the intermediate coupling ranges, however, \( ^3 \Lambda_{1} \) will contain admixtures of other \( \Omega=1 \) states.

**(11) \( \Xi \) States**

The correlation of (\( \Lambda, S \)) coupled \( \Xi \) states with (\( \Omega_C, \omega \))
states having $\Omega=1$ or $0^+$ cannot be made on the basis of qualitative arguments alone. A. Recknagel\textsuperscript{56} has shown that the relative energies of the $\Sigma$ and $\Delta$ states are:

\[ 3^+_u : E = C + a \quad 3^+_u : E = C + a \]

\[ 1^+_u : E = C + 2b \]

\[ 3^-_u : E = C - a \quad 1^-_u : E = C - a + 4c \]

where

\[ a = \int \frac{\bar{\Pi}_u(1)\Pi_u(2)}{r_{12}} \frac{1}{\bar{\Pi}_u(1)\Pi_u(2)} d\tau_1 d\tau_2 \]

\[ b = \int \frac{\bar{\Pi}_u(1)\Pi_u(2)}{r_{12}} \frac{1}{\bar{\Pi}_u(1)\Pi_u(2)} d\tau_1 d\tau_2 \]

\[ c = \int \frac{\bar{\Pi}_u(1)\Pi_u(2)}{r_{12}} \frac{1}{\bar{\Pi}_u(1)\Pi_u(2)} d\tau_1 d\tau_2 \]

and

\[ a, b, c > 0. \]

It follows that the lowest state of the $(-g)^3_u$ configuration of $\text{CO}_2$ is $3^-_{1,0}^-$ in $(\cdot \cdot S)$ coupling and because of the non-crossing rule this must correlate with an $(\cdot \cdot C^-)$ coupled state derived from the $2^+_{3\Pi}^g$ core.

Recent unpublished calculations by N. Wisker and al.\textsuperscript{57} on the lower excited states of $\text{CO}_2$ show that the $1^+_{1,0}^-$ state lies at much higher energy than any of the other states derived from a $(-g)^3_u$ configuration and that the $1,3^-_{1,0}^-$ states lie below $1^-_{1,0}$. 
Correlation of States Between Ideal (\( \Lambda S \)) and (\( \Pi C_{nu} \)) Couplings for a (\( \eta g_{nu} \)) Configuration.
3.2 Selection Rules for Rydberg Transitions in CO₂

(i) General Selection Rules in \((\Lambda, S)\) and \((\Omega_c, \omega_c)\) coupling schemes.

Electromagnetic radiation constitutes dipole, quadrupole and higher electric and magnetic radiation fields. If an electromagnetic wave encounters a molecule in an electronic state \(\psi_e\), the interaction of the electric or magnetic vector of the radiation field with the electric moments of the molecule can lead to absorption of radiation as the molecule undergoes a transition to a state of higher energy \(\psi_{e''}\). The probability of a transition between \(\psi_e\) and \(\psi_{e''}\) depends on the square of the magnitude of the matrix elements of the electric or magnetic multipole moments, \(P\).

\[
R_{e' e''} = \int \psi_{e''} P \psi_e \, d\tau_e
\]

A transition is said to be allowed if \(R_{e' e''}\) is different from zero and forbidden if \(R_{e' e''} = 0\). Selection rules are the conditions under which transitions are allowed or forbidden.

Electric dipole transitions are the most important in the u-v or vacuum u-v region of the electromagnetic spectrum. If the dependence of \(\psi_e\) on the nuclear co-ordinates is neglected (Born-Oppenheimer approximation) the electric dipole transition probability is determined by:

\[
R_{e' e''}(Q_0) = \int \psi_{e''}(q, Q_0) M_e \psi_e(q, Q_0) \, d\tau_e
\]

where \(q\) stands for all the electronic co-ordinates, and \(Q\) for all the nuclear co-ordinates. \(M_e\) is the electric dipole
moment vector.

An electronic transition between $\psi_e$ and $\psi_e^\prime$ is allowed if the product $\psi_e \psi_e^\prime$ belongs to the same symmetry species ($\Gamma$) as one of the components of $M_e$, or equivalently if:

$$\Gamma(\psi_e) \otimes \Gamma(\psi_e^\prime) \otimes \Gamma(M_e)$$

is totally symmetric.

This requirement leads to certain general selection rules for electric dipole transitions in molecules belonging to the $D_{\infty h}$ point group,54 which is the symmetry group of linear $XY_2$ molecules.

Table 3.1 gives these selection rules for transitions from the $^1\Sigma_g^+ (0^+)$ ground state of $CO_2$ to states derived from the excited $(\pi_g)^3 \sigma_u$ or $(\pi_g)^3 \pi_u$ configuration in ($\Lambda, S$) or ($\Sigma_C, \omega$) coupling. In addition to these rules there is the general selection rule valid for any coupling scheme:

$$\mathbf{g} \leftrightarrow \mathbf{u} ; \mathbf{g} \leftrightarrow \mathbf{u} ; \mathbf{u} \leftrightarrow \mathbf{u}.$$  

The table shows that the only transition from the ground state of $CO_2$ to states derived from $(\pi_g)^3 \sigma_u$ allowed throughout the range of coupling is:

$$^1\Sigma^+_1 \rightarrow ^1\Sigma_g^+ (0^+)$$

At intermediate coupling $^1\Sigma^+_1$ mixes with $^3\Pi_1$ and the transition $^3\Pi_1 \rightarrow ^1\Sigma_g^+ (0^+)$ will be allowed, and borrow intensity from $^1\Pi_1 \rightarrow ^1\Sigma_g^+ (0^+)$. In the limit of ideal ($C, \omega$) coupling the transitions
Table 3.1

Selection Rules for Rydberg Transitions in CO₂

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(Λ, S)</th>
<th>States</th>
<th>ΔΛ=0,±1</th>
<th>ΔS=0</th>
<th>++→ΔΩ=0,±1</th>
<th>0⁺→0⁺</th>
<th>(n C, ω)</th>
<th>States</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Π₁</td>
<td>a</td>
<td>a</td>
<td>f</td>
<td>a</td>
<td></td>
<td></td>
<td>(1/2,1/2)₁</td>
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</tr>
<tr>
<td>3Π₀⁺</td>
<td>a</td>
<td>f</td>
<td>a</td>
<td>a</td>
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<td>(1/2,1/2)₀⁺</td>
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<td>(1/2,3/2)₂</td>
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<td>(1/2,3/2)₁</td>
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<td>(3/2,3/2)₀⁺</td>
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<td>(3/2,1/2)₁</td>
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</tbody>
</table>
$^1\Gamma_1 + ^1\Sigma^+ (0^+)$ and $^3\Pi_1 + ^1\Sigma^+ (0^+)$ will have equal intensity.

Transitions to $(\frac{1}{2}, \frac{1}{2})_0^+$ are apparently allowed in ideal $(\Omega_C, \omega)$ coupling but the wavefunction for this state is the same as for $^3\Pi_0^+$ transitions to which are spin forbidden in $(\Lambda, S)$ coupling. However it is possible that extraconfigurational mixing with nearby $0^+$ states may make transitions to $(\frac{1}{2}, \frac{1}{2})_0^+$, $(^3\Pi_0^+)$ weakly allowed.

The only transition from the ground state of CO$_2$ to states derived from the $(\pi_g)^3\pi_u$ configuration allowed throughout the range of coupling is:

$^1\Sigma_u^+ (0^+) + ^1\Sigma_g^+ (0^+)$

However inspection of the state wavefunctions shows that $^1\Sigma_0^+$ and $^3\Sigma^+_1$ both consist of $(\frac{1}{2}, \frac{1}{2})_0^+$ in ideal $(\Omega_C, \omega)$ coupling so the transition $^3\Sigma^+_1 + ^1\Sigma_g^+ (0^+)$ will be allowed in intermediate coupling. Transitions from the ground state to $^3\Sigma^-_1$ and $^3\Sigma^-_1$ are also possible close to ideal $(\Omega_C, \omega)$ coupling.

11 Vibronic Interaction

The selection rules based on the equation 3.5

$\langle e'| e \rangle = \int \psi_{e'}^*(q, Q_o) M \psi_e(q, Q_o) d^r_{e'} \neq 0$,

are valid only if it is possible to separate the electronic motion from the nuclear motion and write the molecular wavefunction as a product of two functions one of which depends on the electronic co-ordinates $q$ for fixed nuclear positions $Q$ and the other which depends on the nuclear co-ordinates $Q$, i.e.

$\psi_e = \psi_e(q, Q) \psi_v(Q)$ 3.6
While this separation is usually a good first approximation, the coupling of electronic and nuclear motions must be included to higher order. In this case the selection rule 3.5 must be written as:

\[ R_{e'} \nu_1 e'' \nu_2 = \int \psi_{e'} \psi_{e''} M \psi_{\nu_1} \psi_{\nu_2} \, d\tau_{e' \nu_1} \neq 0 \quad 3.7 \]

and an electric dipole transition between \( \psi_{e'} \) and \( \psi_{e''} \) is allowed if the product of the vibronic species belongs to the same species as one of the components of the dipole moment \( M \). (The symmetry species of the vibronic wavefunction \( \psi_{e'} \) is the direct product of the species of \( \psi_e \) and \( \psi_\nu \) even when the product resolution 3.6 does not hold). Because of the change of the selection rule 3.5 to selection rule 3.7 in a higher approximation, certain transitions which are forbidden by 3.5 can become allowed by 3.7 if suitable vibrations are excited. For example a \( ^1\Pi_g \rightarrow ^1\Sigma^+ \) transition is forbidden by the rule \( g \rightarrow g \) but if one quanta of a bending \( ^1_u \) vibration is singly excited in the ground or excited electronic state, transitions are allowed between certain vibronic states. 54

3.3 Changes in Geometry in the excited state

It is well established that \( \text{CO}_2 \) and \( \text{CO}_2^+ \) are linear in the equilibrium conformation of their ground states 54 and so far in this thesis it has been assumed that \( \text{CO}_2 \) is also linear in the equilibrium conformation of its Rydberg excited states. However, A.D. Walsh 58 has shown that \( \text{CO}_2 \) is probably bent in
certain sub-Rydberg excited states and it is possible that 
\( \text{CO}_2 \) is also bent in some Rydberg states. The excited states
of bent \( \text{CO}_2 \) cannot be classified under the \( \text{D}_{\infty h} \) point group
but transform like the irreducible representations of the
\( \text{C}_{2v} \) point group, and the selection rules given on p.94 are
no longer valid. It is therefore worthwhile investigating if
any \( \text{CO}_2 \) Rydberg states are in fact bent in their equilibrium
conformation.

It was shown in Chapter 1 of this thesis that the
factorisation of the wavefunction, \( \psi_{\text{Mol}} = \psi_{\text{ion}} \psi_{\text{Ryd}} \), is a good
approximation for Rydberg States. It follows that the energy,
\( E_{\text{CO}_2^+} \) of a Rydberg state of \( \text{CO}_2 \) is equal to the sum of the
energy of the ion-core, \( E_{\text{CO}_2^{++}} \), and the energy of the Rydberg
electron, \( E_{\text{Ryd}} \), i.e.

\[
E_{\text{CO}_2^+} = E_{\text{CO}_2^{++}} + E_{\text{Ryd}}
\]

Because \( \text{CO}_2^+ \) is linear in its equilibrium conformation, bending
\( \text{CO}_2^+ \) will increase the energy of the ion and only if \( E_{\text{Ryd}} \)
decreases on bending can the equilibrium conformation of the
Rydberg state be bent.

The equilibrium internuclear angle, \( \Theta \), of a Rydberg
state of \( \text{CO}_2 \) is determined by the condition that \( E_{\text{CO}_2^+} \) is
a minimum, and

\[
\left( \frac{\partial E}{\partial \Theta} \right)_{\text{opt}} = 0
\]
Therefore, from equation 3.8
\[
\frac{\partial E_{\text{CO}_2^+}}{\partial \theta} \theta_e = - \left( \frac{\partial E_{\text{Ryd}}}{\partial \theta} \right) \theta_e
\]
\[3.10\]

The bending force constant of CO$_2^+$ is,
\[
k_{\text{CO}_2^+}(\theta) = \frac{\partial^2 E_{\text{CO}_2^+}}{\partial \theta^2}
\]
\[3.11\]

so that,
\[
\frac{\partial E_{\text{CO}_2^+}}{\partial \theta} \theta_e = \int_{\theta=0}^{\theta=180^\circ} k_{\text{CO}_2^+}(\theta) d\theta
\]
\[3.12\]

Then assuming that $E_{\text{Ryd}}$ is a linear function of $\theta$,
\[
\left( \frac{\partial E_{\text{Ryd}}}{\partial \theta} \right) \theta_e = \left( \frac{\partial E_{\text{Ryd}}}{\partial \theta} \right) \theta=180^\circ = - \int_{\theta=0}^{\theta=180^\circ} k_{\text{CO}_2^+}(\theta) d\theta
\]
\[3.13\]

Equation 3.13 allows $\theta_e$ to be determined from the behaviour of $E_{\text{Ryd}}$ on bending linear CO$_2$, provided the bending force constant of CO$_2^+$ is known as a function of $\theta$.

Values of $E_{\text{Ryd}}$ for Rydberg states of linear CO$_2$ are given to a first approximation by the model potential calculations discussed in Chapter 2 of this thesis. Symmetry rules for the resolution of $D_{\text{sh}}$ species into those of $C_{2v}$ can be applied to the calculated united-atom Rydberg orbitals to obtain symmetry components of Rydberg orbitals in bent CO$_2$. 

---

[Diagram showing $D_{\text{sh}}$ and $C_{2v}$ symmetries]
\[ D_{\text{orthogonal}} \quad C_{2v} \]

\[ n\sigma_g \quad n\sigma_1 \]
\[ n\pi_u \quad n\pi_2 \]
\[ n\pi_u \quad n\pi_1 \]
\[ n\pi_u \quad n\pi_1 \]

The symmetry splittings of united-atom orbitals due to the non-spherical part of the potential can be divided into two contributions:

\[
\mu_{\text{c.s.}} = \mu_{\text{in}} + \mu_{\text{out}} \quad \text{(see p. 61)} \quad 3.14
\]

(i) Outside the ion-core

Because Rydberg Mo's are like phase-shifted hydrogen orbitals outside the ion-core, \( \mu_{\text{out}} \) is similar to \( \mu_{\text{out}} \) for a hydrogen orbital in a point-charge distribution with the same geometry as the core.

The one-electron perturbation calculations of H. Hosoya\(^{32}\) can be used to estimate the splitting pattern of hydrogenic orbital components in going from \( D_{\text{orthogonal}} \) to \( C_{2v} \) point-charge distributions. The most important feature of these splittings is the behaviour of the \( n\pi_u \) orbital on bending the ion-core.

The matrix elements involving \( p_x \) orbitals are independent of \( \theta \), so \( n\pi_x u \) and \( n\pi_b \) are without changing energy. On the other hand, \( n\pi_y u \) and \( n\pi_z u \) are both functions of \( (1 - \cos 2\theta) \), while the second-order term \( n\pi_y u \) perturb \( n\pi_z u \) as a function of \( \sin 2\theta \). The components \( n\pi_z \) and \( n\pi_y \) are mixed as the molecule is bent forming two new orbitals which transform as
a₁ and b₂ under the symmetry operations of the C₂ᵥ point group.

\[ npa₁ = nπ_y u \sin \beta + nπ_x u \cos \beta \]
\[ npb₂ = nπ_x u \sin \beta - nπ_y u \cos \beta \]

When \( \beta = 45^\circ \), equivalent to a bond angle \( \theta = 90^\circ \), \( npa₁ \) and \( npb₂ \) have the same energy, midway between the energies of \( nπ_u \) and \( nπ_u \) in the linear molecule.

In the bent conformation of CO₂, \( nπ_u \) and \( npa₁ \) can mix (2nd order perturbation) and will repel each other. However, because the energy interval \( E(nπ_u - nπ_u) \) is quite large compared to \( E(nπ_u - nπ_u) \), this repulsion will be small relative to the lowering of \( nπ_u (a₁) \) on bending.

(ii) Inside the ion-core.

Model wavefunctions do not give accurate representations of "true" Rydberg orbitals inside the ion-core because of the nature of the model potential method (See Chapter 2). The form of a Rydberg orbital inside the core is governed by the orthogonality constraints imposed on the Rydberg orbital by its real core precursors. The M.O. core precursors for the \( nσ_q \), \( nπ_u \) and \( nπ_u \) Rydberg orbitals of CO₂ are given in Table 3.II. (These do not include core MO's composed of ls orbitals).

<table>
<thead>
<tr>
<th>Rydberg Orbital</th>
<th>M.O. Core Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>( nσ_q )</td>
<td>3σ_g, 4σ_g</td>
</tr>
<tr>
<td>( nπ_u )</td>
<td>2σ_u, 3σ_u</td>
</tr>
<tr>
<td>( nπ_u )</td>
<td>1π_u</td>
</tr>
</tbody>
</table>
Inside the core a Rydberg orbital takes the form of a linear combination of core precursor M.o's. e.g.

\[ \phi_{3\sigma_g}^{(\text{core})} = c_1 \ 3\sigma_g + c_2 \ 4\sigma_g \]

Each core M.o acts like a loop creating function with small coefficients, \( c_1 \) and \( c_2 \), in the complete Rydberg orbital. Hence the core part of a Rydberg orbital will behave in the same way as it's real core precursors on bending the molecule.

The variation of orbital energies of an \( XY_2 \) molecule in going from the linear (\( \theta = 180^\circ \)) to the bent (\( \theta = 90^\circ \)) conformation is usually represented in a Walsh diagram\(^{54,58}\).

S.P. McGlynn et al.\(^{59}\) have given a semi-quantitative Walsh diagram for \( CO_2 \) which indicates that the behaviour of \( CO_2 \) M.o's on bending the molecule is as follows:

\[ \begin{align*}
3\sigma_g & \quad 4\sigma_g \quad \text{Stabilized} \\
2\pi_u & \quad \text{Destabilized} \\
3\pi_u & \quad \text{Slightly stabilized} \\
1_u \left\{ \begin{array}{l}
^{a_1} \\
^{b_1} \end{array} \right. & \quad \text{Slightly destabilized} \\
\end{align*} \]

Unchanged

By analogy with equation 3.14, the total change in orbital energy, \( \Delta E \), on bending the molecule is given by,

\[ \Delta E = \Delta E^{\text{in}} + \Delta E^{\text{out}} \quad 3.15 \]

The \( \Delta E \) are negative when the orbital energy is lowered on bending the molecule. A summary of the signs of \( \Delta E^{\text{in}} \) and \( \Delta E^{\text{out}} \)
with the resultant sign of $\Delta E$ is given in Table 3.3.

Table 3.3

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$\Delta E_{\text{out}}$</th>
<th>$\Delta E_{\text{in}}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ns$g$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>np$u$</td>
<td>+</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>np$u_{a_1}$</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>np$u_{b_1}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

From the total change in orbital energy on bending the molecule to $\theta = 90^\circ$, it is possible to estimate that for both $3s\sigma_g(a_1)$ and $3p\pi_u(a_1)$,

$$\frac{3E_{\text{Ryd}}}{\theta} = -4 \times 10^{-4} \text{ a.u./deg}$$

If the bending force constant of $\text{CO}_2^+$, $k_{\text{CO}_2^+}$, were known as a function $\theta$, $\theta_e$ could be determined from this estimate of $\frac{3E_{\text{Ryd}}}{\theta}$ using equation 3.13. Unfortunately, $k_{\text{CO}_2^+}(\theta)$ cannot be obtained reliably from force-constant calculations because the bending frequency, $\nu_2$, of $\text{CO}_2^+$ is not an experimentally known quantity. However, a comparison with $k_{\text{CO}_2}(\theta)$ indicates that $\text{CO}_2$ is only slightly bent (i.e., $\theta_e > 170^\circ$) in the $\left(\pi_g\right)^2 3p\pi_u(a_1)$ and $\left(\pi_g\right)^3 3s\alpha_1$ configuration of $\text{CO}_2$.

If $\left(\pi_g\right)^3 3s\sigma_g\left(\text{I}_g\right)$ is slightly bent the forbidden transition,

$$\ldots\left(\pi_g\right)^3 3s\sigma_g\left(\text{I}_g\right) + \text{I}_g^*$$

is actually,

$$\ldots\left(a_2\right)^2 b_2 3s\alpha_1\left(\text{I}_g\right) - \text{I}_g^*$$

which is allowed.
CHAPTER 4
RYDBERG SERIES IN CO₂

4.1 Experimental Studies of the Rydberg Excited States of CO₂

The lower excited states of CO₂ (i.e., states with excitation energies less than the first ionisation potential) have been investigated by optical absorption spectroscopy on several occasions since the pioneering work of T. Lyman in 1908.

A Rydberg series extending from 1120-900 Å and converging to the first ionisation potential of CO₂ at 13.79 ev. was identified in the absorption spectrum by W.C. Price et al. in 1938. Recently several additional series have been found in the region below 1200 Å by Y. Tanaka et al. and their published table of frequencies has been adopted in this thesis. A plot of the absorption coefficient of CO₂ in the region 1670-580 Å has been published by K. Watanabe et al. and gives a useful representation of Tanaka's Rydberg series; this plot is reproduced on p. 122 (Fig. 4.II).

In addition to conventional optical spectroscopy the technique of electron-impact spectroscopy has proved to be useful in the study of molecular excited states; electron impact spectra of CO₂ have been obtained by E.W. Lassettre et al. at different accelerating voltages and scattering angles. At high accelerating voltages (impact
energy \gg \text{excitation potentials} \) and zero scattering angle, energy loss spectra are very similar to optical absorption spectra. However, at low impact energy and high scattering angles optically forbidden singlet-triplet and electric quadrupole transitions increase in intensity relative to optically allowed transitions. This fact can be used to identify spin and symmetry forbidden transitions.

4.2 Theoretical Studies of the Lower Excited States of CO$_2$

Introduction

With the best resolution possible on modern spectrographs the vacuum u-v spectrum of CO$_2$ consists of diffuse bands with no discernible fine structure. Rotational analysis of this type of spectrum is not possible and excited state assignments of absorption bands must be made on the basis of theoretical considerations.

Several ab initio calculations of the excited states of CO$_2$ have been published\(^{66,67,68}\) but none of these has included Rydberg orbitals in the basis set, and consequently a description of only sub-Rydberg states has been obtained. An extended Gaussian basis set containing diffuse Rydberg-like orbitals has been used by N.W. Winter et al.\(^{57}\) in recent unpublished calculations on the lowest five (singlet and triplet) Rydberg states of CO$_2$.

In Chapter 2 of this thesis a semi-empirical model potential approach to the calculation of Rydberg series in small polyatomic molecules has been developed and its applications
to CO₂, CS₂ and CSe₂ will be discussed below. First however, a brief comparison of this type of semi-empirical calculation with the ab initio calculations typified by those of Winter et al.⁵⁷ will be made.

Semi-empirical calculations based on model potentials rather than self-consistent fields are approximations to ab initio calculations with self-consistent field Hamiltonians. However, the elimination of core wavefunctions in model potential calculations gives the approach at least two practical advantages over ab initio methods:

1) The model potential method is numerically simple and requires only a few minutes of computer time for the calculation of a complete Rydberg series. By contrast ab initio calculations require several hours for the determination of one Rydberg state.

2) Model potential calculations are applicable to any small molecule while ab initio calculations are restricted to molecules containing first-row atoms due to practical limitations on the size of the basis set.

Because part of this thesis deals with molecules containing second and third-row atoms, semi-empirical calculations have been used throughout. Nevertheless the ab initio calculations of Winter et al.⁵⁷ have been useful because they provide assignments of the first members of the nσg, npu and npu Rydberg series of CO₂, and serve to test the accuracy of the model potential derived for CO₂ in this thesis. The extent to which model potential calculations agree with assignments of low lying
CO₂ Rydberg states based on ab initio calculations, establishes the validity of the model potential and justifies its applications to higher Rydberg states.

Model Potential Calculations and the Rydberg Series of CO₂

Prior to the present work the only excited state configuration assignments for the Rydberg series of CO₂ were made by E. Lindholm⁶⁹ on the basis of qualitative arguments on the relative magnitudes of quantum defects. The model potential calculations presented in Chapter 2 of this thesis place Lindholm's qualitative arguments on a quantitative theoretical basis.

Lindholm assumed that Rydberg orbitals are essentially hydrogenic in character with quantum defects, \( \mu(n\ell\lambda) \), depending on the degree of core penetration of the orbital. For linear molecules he assumed quantum defects in the order,

\[
\mu(n\sigma) > \mu(n\rho\sigma) > \mu(n\rho\pi) > \mu(n\delta\sigma) > \mu(n\delta\pi) > \mu(n\delta\delta)
\]

and analysed Tanaka's⁶¹ Rydberg series of CO₂ on this basis. He assigned Main series (1) to \( 1\pi_g \rightarrow n\rho\sigma_u \) and Minor series (1) to \( 1\pi_g \rightarrow n\rho\pi_u \). Minor series (2) was assigned to the forbidden transitions \( 1\pi_g \rightarrow n\delta\pi_q \). No series involving \( n\sigma_q \) orbitals were assigned. Lindholm considered Rydberg series in many diatomic and small polyatomic molecules in a similar manner and acknowledged that the order of \( \mu(n\rho\sigma) \) and \( \mu(n\rho\pi) \) appeared to be reversed in some molecules.
In this thesis it has been shown that the quantum defect of a molecular Rydberg series can be written as (see p44):

\[ \mu_{\text{Mol}} = \mu_{\text{pen}} + \mu_{\text{c.s.}} \]

Lindholm is correct in assuming,

\[ \mu_{\text{Mol}}(n\sigma) > \mu_{\text{Mol}}(n\pi,n\pi) \]

because \(n\sigma\) orbitals are more penetrating than \(n\pi\) orbitals, and the difference in quantum defects between orbitals with different \(l\) is largely determined by \(\mu_{\text{pen}}\). However, Lindholm's arguments do not account for the difference in quantum defects between orbitals with the same \(l\) but different \(\lambda\). Thus, for example, \(p\sigma - p\pi\) splittings are determined by \(\mu_{\text{c.s.}}\) which can be subdivided into contributions from inside and outside the ion-core.

\[ \mu_{\text{c.s.}} = \mu_{\text{c.s.}}^{\text{in}} + \mu_{\text{c.s.}}^{\text{out}} \]

The symmetry splittings of a hydrogenic orbital outside an ion-core with the point-charge distribution of a linear triatomic molecule are such that,

\[ \mu_{\text{c.s.}}^{\text{out}}(n\pi) > \mu_{\text{c.s.}}^{\text{out}}(n\pi) \]

Values for \(\mu_{\text{c.s.}}^{\text{in}}(n\pi)\) cannot be determined by qualitative arguments but it is apparent that \(\mu_{\text{c.s.}}^{\text{in}}(n\pi)\) and \(\mu_{\text{c.s.}}^{\text{in}}(n\sigma)\) are numerically different because \(n\pi\) and \(n\sigma\) orbitals extend over different regions of core space. (See Fig. 4.I).
Fig. 4.1

The approximate form of the

\[ 3p_{\sigma u} \] and \[ 3p_{\pi u} \] CO\(_2\) Rydberg MO's
If $\mu_{c.s.}^{in}(np\sigma) < \mu_{c.s.}^{in}(np\pi)$ it is possible that $p\sigma - p\pi$ splittings can be the reverse of the ordering predicted by Lindholm.

Results

Rydberg series calculated for CO$_2$ using the model potential method developed in Chapter 2 are given in Table 4.1. The relationship of the calculated term values for the first member of each series to Rydberg transitions observed in the CO$_2$ spectrum will now be considered.

(i) 3s$_g$

The 3s$_g$ term of CO$_2$ is calculated to be +0.1175 a.u. corresponding to a quantum defect of 0.95. If 1$\pi_g - n$s$_g$ is weakly allowed in the u-v spectrum of CO$_2$, the calculation predicts the first member of this series should be observed ~1200 Å. In this region of the CO$_2$ spectrum there is a weak absorption system extending from 1400-1200 Å with a maximum at 1330 Å and there is a considerable body of evidence favouring the assignment of this transition to 1$\pi_g - 3$s$_g$. This evidence is as follows:

(i) E.N. Lassettre et al. 63, 64, 65 have shown that the envelope shape of the absorption from 1700-1200 Å in the electron impact energy-loss spectrum changes with scattering angle and impact energy, and suggest this is evidence for changes from a dipole to quadrupole spectrum. The absorption system is attributed to the quadrupole allowed transition 1$\pi_g - 1\pi_g$ which is electric
Table 4.1

Calculated Rydberg Terms for CO₂
(Average of values given in Table 2.4V)

<table>
<thead>
<tr>
<th>n</th>
<th>nσ₀_u (a.u.)</th>
<th>nσ_u (a.u.)</th>
<th>nσ_u (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1175</td>
<td>0.0955</td>
<td>0.0970</td>
</tr>
<tr>
<td>3</td>
<td>0.0518</td>
<td>0.0434</td>
<td>0.0454</td>
</tr>
<tr>
<td>4</td>
<td>0.0293</td>
<td>0.0251</td>
<td>0.0262</td>
</tr>
<tr>
<td>5</td>
<td>0.0189</td>
<td>0.0163</td>
<td>0.0170</td>
</tr>
<tr>
<td>6</td>
<td>0.0131</td>
<td>0.0116</td>
<td>0.0120</td>
</tr>
<tr>
<td>7</td>
<td>0.0097</td>
<td>0.0086</td>
<td>0.0088</td>
</tr>
</tbody>
</table>
dipole allowed if the excited state, $^1\Pi_g$, is slightly bent. 

(ii) S.P. McGlynn et al.$^{59}$ have assigned the 1330 Å transition to $^1\Pi_g - ^1\Sigma_g^+$ with a slightly bent upper state. The Franck-Condon principle for a bent + linear transition predicts that the strongest absorption bands should involve excitation of the upper state bending vibration, $v_2'$. Transitions of this type are subject to very strong rotation-vibration interaction leading to an irregular arrangement of energy levels. McGlynn listed the observed vibrational frequencies of the 1330 Å transition and found that they were "irregular but consisted of a simple progression \(~624 \text{ cm}^{-1}\)". This is close to the bending frequency of the ground state of CO$_2$ (667 cm$^{-1}$). 

(iii) The unpublished calculations of N.W. Winter et al.$^{57}$ on CO$_2$ excited states give a vertical excitation energy for $^1\Pi_g - ^1\Sigma_g^+$ of 9.23 ev corresponding to a transition in the u-v spectrum \(\sim 1350 \text{ Å}\). These calculations show that the $^1\Pi_g$ state has the basic S.C.F. orbital form ...$\pi_g^13\sigma_g^\perp$.

If the 1330 Å transition in the CO$_2$ u-v spectrum is due to ...$\pi_g^13\sigma_g^\perp$ \(\sim 1\Pi_g - ^1\Sigma_g^+\), the $3\sigma_g^\perp$ term value is +1.1634 a.u. compared to a value of +1.175 a.u. determined by the model potential calculation. Clearly the observed $3\sigma_g^\perp$ level is considerably more stable than the calculated level. The difference,

\[ E_{\text{dif}} = E_{\text{obs}} - E_{\text{calc}} = -0.045 \text{ a.u.} \]

between theory and experiment can be accounted for by a number
of factors which have been omitted from the calculation:

(a) Changes in Geometry in the Excited State

In this thesis all Rydberg terms have been calculated for the linear conformation of CO$_2$ although the discussion on pp 96-102 showed that the excited configuration $\pi_g^3 3\sigma_g$ of CO$_2$ is more stable in a slightly bent conformation. This indicates that the transition $\pi_g^3 3\sigma_g (\Pi_g^1 + \Pi_g^1)$ in CO$_2$ corresponds to a bent + linear transition and is fully in accord with the assignments of Lassettre$^{63,64,65}$ and McGlynn$^{59}$ concerning the 1330 Å transition of CO$_2$. However the lowering of the Rydberg term energy of bent CO$_2$ relative to linear $\Pi_g^1$ is small (probably 0.005 a.u.) and accounts for only a small part of $E_{\text{dif}}$.

(b) The Effects of s-d Mixing

The calculation of the n$\sigma_g$ terms of CO$_2$ has been carried out using only s functions and assumes the Rydberg orbital is an exact eigenfunction of $\mathcal{H}_0$. Actually there is probably ~10% s-d mixing (see p.61) in the 3$\sigma_g$ orbital which will lower a 3$\sigma_g$ level calculated without this mixing. However, because the closest d level which can mix with 3$\sigma_g$ is 3$d_g$ and the energy interval 3$\sigma_g - 3$d_g$ is quite large, it can be estimated that the inclusion of s-d mixing will lower the $3\sigma_g$ level by no more than 0.007 a.u.

(c) Bonding Effects

The model potential used in the calculation of CO$_2$ Rydberg terms consists of a superposition of free-atom model
potentials and neglects terms of the type \( V_{AB}(R) \) which arise from the interaction of atomic cores (see p. 46). \( V_{AB}(R) \) allows for the fact that a real molecule does not consist of its constituent free atoms at their equilibrium separations but contains atoms modified by bond formation. In this thesis Rydberg orbitals have been calculated with non-bonding core potentials (i.e. \( V_{AB}(R) \) has been omitted). These will be denoted \( \phi(n\ell\lambda) \), while Rydberg orbitals calculated with bonding cores (\( V_{AB}(R) \) included) will be denoted \( \phi'(n\ell\lambda) \).

The difference between \( \phi(n\ell\lambda) \) and \( \phi'(n\ell\lambda) \) can be estimated qualitatively from the bonding/anti-bonding characteristics of M.O. core precursors. Thus inside the core, \( \phi'(n\sigma_g) \) is bonding, \( \phi'(n\pi_u) \) anti-bonding and \( \phi'(n\pi_u) \) weakly bonding relative to its \( \phi(n\ell\lambda) \) counterpart. If it is assumed that after allowing for neglect of geometry changes and \( l \)-spoiling in the calculation,

\[
E_{\text{dif.}} = E_{\text{obs}} - E_{\text{calc}} = E(\phi'(n\ell\lambda)) - E(\phi(n\ell\lambda))
\]

then for the \( 3\sigma_g \) orbital,

\[
E(\phi'(3\sigma_g)) - E(\phi_{3\sigma_g}) = -0.03 \text{ a.u.}
\]

If the \( 3\sigma_g \) Rydberg electron gives a bonding contribution to \( \text{CO}_2^+ \), the vibrational frequencies \( (\nu)_\text{CO}_2^+ \) of the \( \text{CO}_2^+ \) excited state \( ^1\Sigma_g^+ \) should be higher than the equivalent frequencies, \( (\nu)_\text{CO}_2^+ \), in \( \text{CO}_2^+ \). The ground state frequencies \( (\nu)_\text{CO}_2 \) and \( (\nu)_\text{CO}_2^+ \) are: 54
\( \nu_1 \) \( \nu_2 \) \( \nu_3 \)
\( \text{CO}_2 \) (cm\(^{-1}\))
\( \text{CO}_2^+ \) (cm\(^{-1}\))
1388
667
2349
1280
\( \nu_4 \) 1469

\((\nu_2)^{\text{CO}_2^+}\) has been estimated from a comparison of the behaviour of \( \nu_2 \) for \text{CS}_2 and \text{CS}_2^+ and force constant calculations on \text{CO}_2^+.

According to McGlynn\(^{59}\), \((\nu_2)^{\text{CO}_2}\) for \[ \Pi_g \left( \pi_g \right)^3 \sigma_u \] is 1624 cm\(^{-1}\) which is very close to \( \nu_2 \) for the ground state of \text{CO}_2, and much larger than the estimated value of \((\nu_2)^{\text{CO}_2^+}\).

Thus there is experimental evidence for the prediction that \(3\sigma_u\) is bonding in the \text{CO}_2^+ core and the omission of such bonding effects in the model potential calculation probably accounts for the major part of \(\Sigma\text{dif}\).

(ii) \(3\pi_u\) and \(3p\pi_u\)

The model potential calculation for the lowest \(p\) Rydberg terms, \(T_{nl}\), of \text{CO}_2 gives:

\[ T_{3\pi_u} = 0.0955 \text{ a.u.} \]

\[ T_{3p\pi_u} = 0.0970 \text{ a.u.} \]

This ordering is the reverse of that proposed by E. Lindholm\(^{69}\) and suggests that the correct assignment of Tanaka's\(^{61}\) series is:

Main series (1): \( l = \pi_g \left( n\pi_u \right) \)

Minor series (1): \( l = \pi_g \left( n\pi_u \right) \)

\[ 4:1 \]
If this is the case the calculated npσ_u - npπ_u splittings are too small but this can be accounted for by the neglect of the same factors in the model potential calculation which caused errors in the calculated 3σ_g term. These are:

(i) Geometry changes in the excited state

(ii) l-spoiling

(iii) core bonding effects.

The discussion on pp. 96-102 shows that \((\pi_g)^3 \pi^u_{3p}\) is probably bent while \((\pi_g)^3 \pi_{3p}\) is linear, and the observed \(3p^u\) term will be lowered by \(\approx 0.005\) a.u. relative to a \(3p^u\) term calculated for a linear conformation. This implies that the observed \(p^o - p^π\) splittings are larger than those calculated for linear \(CO_2\).

The effects of l-spoiling on calculated \(3p^o\) levels are smaller than for \(3σ_g\) levels and should not affect the ordering of \(p^o\) and \(p^π\) levels.

Core bonding effects for \(p^o\) orbitals are smaller than those for \(s\) orbitals because \(p\) orbitals are less penetrating than \(s\) orbitals. However, the differences that do exist between \(\langle np^o \rangle\) and \(\langle np^π \rangle\) (see p. 113) are such that observed \(p^o - p^π\) splittings are larger for calculated values of \(E(\pi^o_{np})\) than for \(E(\pi^π_{np})\).

Thus changes in the geometry in the excited state and core bonding effects tend to make \(u(np^o) < u(np^π)\) in \(CO_2\). There is, in any case, additional evidence which favours the
ordering of $p_o$ and $p_w$ levels suggested by the model potential calculation and rules out the ordering proposed by Lindholm.\(^6^9\)

The ab initio calculations of N.W. Winter\(^5^7\) give the term values:

$$T_{3p_u} (^1\Sigma_u^+ \rightarrow) = +0.0996 \text{ a.u.}$$

and

$$T_{3p_u} (^1\Pi_u) = +0.0827 \text{ a.u.}$$

The first terms in Tanaka's series are:

Main series (1) = +0.1034 a.u.

Minor series (1) = +0.0883 a.u.

The ab initio calculations therefore favour assignment 4.1.

Experimental confirmation of this assignment comes from the observed vibrational structure of the absorption bands at 1129 Å and 1088 Å in the CO$_2$ spectrum corresponding to the first members of Tanaka's\(^6^1\) Main series (1) and Minor series (1) respectively. The transition at 1129 Å is part of a broad and complex system of bands extending from 1115 to 1185 Å. The bands are diffuse and show many intervals between 520 and 670 cm$^{-1}$. Like the 1330 Å system of CO$_2$ this is suggestive of a bent upper state and is compatible with the assignment of an excited state configuration $^1\Pi_u \rightarrow ^3\Pi_u$ in a slightly bent conformation. In contrast to the transition at 1129 Å the band at 1088 Å is very sharp and shows little vibrational structure; this is to be expected for a state derived from a
$3\sigma_u$ Rydberg orbital which is anti-bonding with respect to $\text{CO}_2^+$ and destabilized on bending.

The higher members of the $1\pi_g + n\ell\lambda$ Rydberg series of $\text{CO}_2$

(i) $n\sigma_g$ and $n\lambda_g$ series

As $n$ increased along the $1\pi_g + n\ell\lambda$ Rydberg series of $\text{CO}_2$ the core bonding effects mentioned in the previous section should diminish because of the diminishing relative amplitude of the innermost loops of the Rydberg orbital $\phi(n\ell\lambda)$. At the same time the $\ell$-spoilng of $\phi(n\ell\lambda)$ decreases and the excited state geometry approaches the linear geometry of the ion-core. For these reasons the model potential calculations used in this thesis should give better agreement with observed term values for higher members of Rydberg series than for the first members of the series.

The calculation predicts $1\pi_g - 4\sigma_g$ should be observed $\sim 1004$ Å ($99560$ cm$^{-1}$) in the $\text{CO}_2$ spectrum, while a quantum defect equal to that observed for the $3\sigma_g$ term would place the $1\pi_g - 4\sigma_g$ transition $\sim 1036$ Å ($96560$ cm$^{-1}$). Transitions due to $1\pi_g - 3\delta_g$ should also be observed in this region of the $\text{CO}_2$ spectrum. If a $3\delta_g$ orbital is non-penetrating (quantum defect $= 0$), $1\pi_g - 3\delta_g$ should be observed $\sim 1010$ Å and Lindholm$^{69}$ has assigned the band observed at 1007 Å in the $\text{CO}_2$ spectrum to this transition. Because $3\delta_g$ and $3\pi_g$ are more penetrating than $3\delta^g_g$, $1\pi_g - 3\delta^{\pi g}_g$ will be to the red
of $1\pi_g + 3d\delta_g$ in the CO$_2$ spectrum and $4s\sigma_g - 3d\sigma_g$ mixing will push $3d\sigma_g$ to the red of $3d\pi_g$.

There are many transitions observed in the CO$_2$ spectrum between 1000 and 1080 Å, and an assignment of each band is not possible; the following approximate scheme is proposed:

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed Bands (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\pi_g + 3d\sigma_g$</td>
<td>1040-1080</td>
</tr>
<tr>
<td>$1\pi_g + 3d\pi_g$</td>
<td>1035</td>
</tr>
<tr>
<td>$1\pi_g + 3d\delta_g$</td>
<td>1007</td>
</tr>
<tr>
<td>$1\pi_g + 4s\sigma_g$</td>
<td>1000-1040</td>
</tr>
</tbody>
</table>

The calculation predicts $1\pi_g + 5s\sigma_g$ should be observed in the CO$_2$ spectrum ~956 Å (104600 cm$^{-1}$). On this basis, the group of bands observed in this region 955-965 Å are assigned to $1\pi_g + 5s\sigma_g$ and $1\pi_g + 4d\lambda_g$. However, the resolution of published spectra in this region is insufficient to allow the different $\lambda$ components of the d series to be assigned to particular bands in the spectrum.

(ii) np$^\pi_u$ and np$^\pi_u$ series

The selection rules for electric dipole transitions in CO$_2$ indicate that the strongest Rydberg series converging to the first ionisation potential of CO$_2$ should be due to transitions of a valence $1\pi_g$ electron to an np$^\pi_u$ orbital.

The Rydberg series identified by W.C. Price et al. in
the 1120-900 Å region of the CO₂ spectrum has been resolved by Tanaka et al., at wavelengths longer than 930 Å, into four component transitions with similar intensity for each n. Tanaka grouped these four components into three Rydberg series as follows:

Main series (1) - two transitions
Main series (2) - one transition
Minor series (1) - one transition

In Chapter 3 it was shown that of the possible transitions from the CO₂ ground state to the manifold of states derived from the excited configuration \( (\pi_g)^3 \) npu, only \( 1_\Sigma_u^+ \) \( \rightarrow \) \( 1_\Gamma_g^+ \) and \( 1_\Pi_u \) \( \rightarrow \) \( 1_\Sigma_g^+ \) are allowed in \((\Lambda,S)\) coupling, while the additional transitions \( 3_\Sigma_0^+ \) \( \rightarrow \) \( 1_\Sigma_g^+ \) and \( 3_\Pi_1 \) \( \rightarrow \) \( 1_\Gamma_g^+ \) become allowed on going over to \((\Omega,C')\) coupling.

The ab initio calculations of N. Winter et al.57 give \( E(1_\Sigma^- \rightarrow 3_\Pi^-) \approx 320 \text{ cm}^{-1} \) for states derived from the \((\pi_g)^3 3\Pi_u \) configuration of CO₂ and the doublet splitting of the ground state of CO₂⁻ is \( \approx 160 \text{ cm}^{-1} \). Consequently the intensity ratio, \( I(3_\Sigma^-) \) should be \( \approx 2:1 \) for the first members of the \( 1_\Sigma^- \) \( \rightarrow \) npu \( 1_\Sigma^- \) series. For higher members of the series \( I(3_\Sigma^-) \approx 1 \) as ideal \((\Omega,C')\) coupling is approached. Similar behaviour is expected for the \( 1_\Sigma_u^+ \) and \( 3_\Gamma_u \) components of the \( 1_\Pi^- \) \( \rightarrow \) npu series. Hence that Tanaka's Main series (1) and (2) and Minor series (1) constitute four component transitions of similar intensity for
each \( n \) can be accounted for by assuming these series are due to the transitions:

\[
1\pi_g + np\sigma_u \quad \{^2\Pi_1(1) \}\text{ and}
\]

\[
1\pi_g + np\pi_u \quad \{^1\Sigma^+_u(0^+) \}
\]

and that, for \( n > 3 \), the excited states are \((\Omega, \omega)\) coupled.

Inspection of the spectrum of \( \text{CO}_2 \) in the region 1150-900 Å shows many weak transitions in addition to the principal components assigned by Tanaka to Rydberg series. Tanaka groups some of these weaker transitions into "vibration series" but it is also possible that some of these absorption bands are due to transitions to \((\Omega, \omega)\) coupled states with \( \Omega = 1 \) or \( 0^+ \) which are weakly allowed through intra and extra configurational state mixing. Detailed excited state symmetry assignments of these bands will require extensive C.I. calculations of the higher Rydberg states of \( \text{CO}_2 \) which are currently not available.

Excited state configuration assignments of Tanaka's series have been made by E. Lindholm who assigned Main series (1) to:

\[
1\pi_g + np\sigma_u \quad (\mu \approx 0.71),
\]

and Minor series (1) to:

\[
1\pi_g + np\pi_u \quad (\mu \approx 0.56),
\]
These assignments were made on the basis of qualitative arguments which have been discussed on pp. 106-107 of this thesis. It was shown that Lindholm's assignments are probably correct for series with different $\lambda$ but are unreliable for series with the same $\lambda$ and different $\lambda$.

The model potential calculations developed in this thesis and the ab initio calculations of N. Winter show that,

$$\mu(3p\sigma) < \mu(3p\pi)$$

in contrast to Lindholm's assignments. For the higher members of the $1^\pi_g \rightarrow n\pi_u$ series the model potential calculations presented in this thesis constitute the only theoretical studies available and indicate that the ordering,

$$\mu(n\sigma) < \mu(n\pi)$$

is maintained along the series. It is therefore probable that Tanaka's Main series (1) and (2) are due to:

$$1^\pi_g \rightarrow n\pi_u$$

and Minor series (1) to:

$$1^\pi_g \rightarrow n\sigma_u$$

A comparison of calculated terms with Tanaka's series is given in Table 4.II. The calculated $n\sigma_u - n\pi_u$ splittings are too small but an explanation of this has already been given for the $n=3$ terms and applies to higher terms (see pp. 114 - 117).
Fig. 4.11

CO$_2$ Spectrum from 1000-1400 Å Showing $1^u_\pi$ + πλ Assignments

Wavelength (Å)
### Table 4.II

A Comparison of Some Calculated and Observed Rydberg Series in CO₂

<table>
<thead>
<tr>
<th>Main Series (1)</th>
<th>Observed Series (a.u.)</th>
<th>Calculated Series (a.u.)</th>
<th>npσ_u</th>
<th>npπ_u</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1034</td>
<td>.1026</td>
<td>.0883</td>
<td>.0955</td>
<td>.0970</td>
</tr>
<tr>
<td>.1008</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.0486</td>
<td>.0461</td>
<td>.0425</td>
<td>.0434</td>
<td>.0454</td>
</tr>
<tr>
<td>.0482</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.0282</td>
<td>.0277</td>
<td>.0252</td>
<td>.0251</td>
<td>.0262</td>
</tr>
<tr>
<td>.0278</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.0186</td>
<td>.0186</td>
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<td>.0163</td>
<td>.0170</td>
</tr>
<tr>
<td>.0183</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.0127</td>
<td>.0125</td>
<td>.0118</td>
<td>.0116</td>
<td>.0120</td>
</tr>
<tr>
<td>.0125</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.0095</td>
<td>.0093</td>
<td>.0088</td>
<td>.0086</td>
<td>.0088</td>
</tr>
</tbody>
</table>
CHAPTER 5  
RYDBERG SERIES IN CS₂

5.1 *Previous Experimental and Theoretical Work*

The vacuum u-v spectrum of CS₂ was first investigated by W.C. Price et al.⁷⁰ in 1938. Price grouped many of the observed absorption bands in the region from 1400-1200 ˚A into two Rydberg series converging to limits separated by 436 cm⁻¹, the doublet separation of the ground state, ²Σ⁺, of CS₂⁺. The CS₂ vacuum u-v spectrum was reinvestigated in 1960 by Y. Tanaka et al.⁷¹ at wavelengths below 1600 ˚A and Price's Rydberg series were confirmed.

J.B. Hasted et al.⁷² have obtained electron energy-loss spectra of CS₂ and grouped most of the observed energy-loss peaks at energies less than 11 e.v.(88, 700 cm⁻¹) into four Rydberg series, two of which correspond to those of Price et al. Hasted proposed Rydberg orbital assignments for these four series and, to date, the only other orbital assignments of Rydberg transitions in CS₂ have been made by S.P. McGlynn⁵⁹ et al. who identified and assigned seven Rydberg series.

Both Hasted⁷² and McGlynn⁵⁹ based their Rydberg orbital assignments on the size of the quantum defect for a particular series and it was shown in Chapter 4 that assignments made in this way, by E. Lindholm⁶⁹ for the Rydberg series of CO₂ were erroneous in certain cases. However, quite apart from the absence of any theoretical justification of the assignments
of Hasted and McGlynn—the assignments of these two authors are quite different and further work is obviously needed.

In the following pages the Rydberg spectrum of CS₂ in the region from 2000 to 1200 Å will be reanalysed and the assignments made will be compared with those of Hasted and McGlynn.

5.2 Model Potential Calculations of the Rydberg Series of CS₂

The model potential calculations developed in Chapter 2 were used to estimate term values for the σ₉ną, np₉u and np₄u Rydberg series in CS₂. The calculated term values are listed in Table 5.1. These calculations constitute the only theoretical studies on the Rydberg series of CS₂ available to date, and form the basis of the analysis of the CS₂ spectrum presented in this thesis.

Because CS₂ has 16 valence electrons it is valence isoelectronic to CO₂ and similarities between the electronic spectra of CS₂ and CO₂ should exist. For the same reason there should be a correlation between observed and calculated term values in CO₂ and CS₂. In particular, two important trends which were observed in the model potential calculations on CO₂ (Sec pp. 109) should also be found in the calculations on CS₂.

(i) Calculated nσ₉ną term values are smaller than the observed nσ₉ną terms especially for the lower members of series.

(ii) Calculated np₄u term values are close to observed np₄u terms, but calculated n₁₅ - n₁₇ splittings are too small.
General Discussion of Results

A comparison of the calculated $ns^q_g$, $np^q_u$ and $np^{q+1}_u$ term values for $CO_2$ (table 4.I) and $CS_2$ (table 5.I) shows that the calculated $CS_2$ term values are all smaller than the corresponding $CO_2$ term values but the difference is never more than 20% between terms. This indicates that the value of the effective quantum number, $n^*$, for the lowest term of a particular series in $CS_2$ is similar to the value of the lowest term of the equivalent series in $CO_2$. At the same time the principal quantum number, $n$, of the Rydberg orbital, $\phi(n\ell\lambda)$, in $CO_2$ must be increased by unity in $CS_2$ if $\phi(n\ell\lambda)$ has real core precursors in the separated atoms. Hence for $ns^q_g$ and $np^q_u$ series in $CO_2$ and $CS_2$,

$$n^*_{\ell\lambda}(CO_2) = n - \mu_{\ell\lambda}(CO_2)$$

and

$$n^*_{\ell\lambda}(CS_2) = n + 1 - \mu_{\ell\lambda}(CS_2)$$

Then because,

$$n^*_{\ell\lambda}(CO_2) = n^*_{\ell\lambda}(CS_2),$$

$$\mu_{\ell\lambda}(CS_2) = \mu_{\ell\lambda}(CO_2) + 1 \quad \ell < 1$$

On the other hand, for $nd^q_g$ and $nf^q_u$ series,

$$\mu_{\ell\lambda}(CS_2) = \mu_{\ell\lambda}(CO_2) - 1 \quad \ell > 1$$

Because the internuclear separations in $CS_2$ are larger than in $CO_2$, $\lambda$ splittings may be larger in $CS_2$ than in $CO_2$. 
but nevertheless, for terms with the same \( n \), \( \lambda \) splittings will certainly be smaller than \( l \) splittings for \( \text{CS}_2 \) Rydberg terms.

With these facts in mind it may be concluded that the ordering of Rydberg terms in \( \text{CS}_2 \) is similar to \( \text{CO}_2 \) and is probably:

\[
4s_{0u}^g > 4p_{1u}^\pi > 4p_{0u}^\sigma > 3d_{1u}^\pi = 3d_{0u}^\pi > 3d_{0g}^\pi > 3d_{0g}^\delta
\]

\[
> 5s_{0u}^g > 5p_{1u}^\pi > 5p_{0u}^\sigma > 4d_{1u}^\pi > 4d_{1u}^\delta > 6s_{0g}^\pi > 6d_{0g}^\pi > 4f_{0u}^\pi > \ldots \text{etc.}
\]

This compares with McGlynn's ordering based on his assignment of \( \text{CS}_2 \) Rydberg transitions:

\[
4s_1 > 3d_1 > 4p_1 > 3d_2 > 3d_3 > 4s_2 > 5s_1 > 4p_2 > 5p_1 > 4d_1 \ldots \text{etc.}
\]

where the subscripts label different symmetry components of terms with the same \( \lambda \).

McGlynn does not explain why two \( \pi_g^\pi \) = \( n\sigma_g^g \) and two \( \pi_q^\pi \), \( \pi_u^\pi \) series should be observed in \( \text{CS}_2 \) although presumably the two \( p \) series are the singlet components of \( \pi_g^\pi \) = \( n\sigma_u^g \) and \( n\sigma_u^u \) series. However, the existence of two \( \pi_q^\pi \) = \( n\sigma_q^g \) series can only be rationalised in terms of transitions to singlet and triplet components of the same excited state configuration \( \ldots (\pi_q^\pi)^3 n\sigma_q^g \). In this case McGlynn's assignment of the \( \pi_q^\pi \) = \( n\sigma_q^g \) series in \( \text{CS}_2 \) implies that the singlet-triplet interval for the \( (\pi_q^\pi)^3 4\sigma_q^g \) configuration is \( \sim 12,286 \text{ cm}^{-1} \).

The Rydberg states of \( \text{CS}_2 \) should be closer to ideal (\( \ldots \))
coupling than ideal \((\Lambda, S)\) coupling and singlet-triplet
intervals should be similar to, but greater than, the spin-
orbit coupling constant, \(\tilde{A}\), for \(\text{CS}_2^+\). For \(\text{CS}_2^+\) \(\tilde{A}\) is 436 \(\text{cm}^{-1}\)
so that McGlynn's\(^{59}\) singlet-triplet interval is clearly
unacceptable.

McGlynn's\(^{59}\) Rydberg assignments are unsatisfactory
in other respects. For example, a non-penetrating \(3d\gamma\)
Rydberg electron should have a term value \(\sim 12,200 \text{ cm}^{-1}\). Hence
the transition \(\pi_g \rightarrow 3d\lambda g\) (non-penetrating) in \(\text{CS}_2\) should be
observed at an energy \(\sim (81,500 \pm 12,200)\) or \(\sim 69,300 \text{ cm}^{-1}\),
corresponding to a wavelength \(\sim 1443 \text{ Å}\) in the \(\text{CS}_2\) spectrum.
Transitions to a penetrating \(3d\lambda g\) orbital must lie to the red of
1443 Å, but certainly no higher than the \(\pi_g \rightarrow 4p\lambda u\) transition.

McGlynn assigns the \(\text{CS}_2\) band at 1595.5 Å to a \(\pi_g \rightarrow 4p\lambda u\)
transition and the 1612 Å band to \(\pi_g \rightarrow 3d\lambda g\). This assignment
is therefore unacceptable and in addition gives \(\pi_g \rightarrow n\delta g\)
series with very poor fits to Rydberg formulae.

Hasted et al.\(^{72}\) do not assign any \(\pi_g \rightarrow n\delta g\) series in
their work on \(\text{CS}_2\); the assignments that are made by these
authors are in accord with the ordering of terms predicted by
the calculations in the present work except that the \(n\rho\sigma\) and
\(n\sigma\) terms are reversed. This is similar to the situation in
\(\text{CO}_2\) where E. Lindholm\(^{69}\) assigned certain \(\text{CO}_2\) series to \(\pi_g \rightarrow n\rho\lambda u\)
in such a way that,

\[ u(n\rho\sigma u) > u(n\rho\pi u); \]
but model potential calculations and independent ab initio calculations favoured

\[ \mu(n\pi_u) > \mu(n\sigma_u) \]

Neither Lindholm nor Hasted were able to supply any evidence for favouring the ordering of \( n\pi_u \) terms they selected.

In the following pages we shall consider in detail the assignment of individual \( CS_2 \) Rydberg transitions and, where possible, supply spectroscopic evidence for assignments based on model potential calculations.

(i) \( 4s\sigma_g \)

The calculated \( 4s\sigma_g \) term value in \( CS_2 \) was 0.1039 a.u. and comparison with \( CO_2 \) results indicates that the observed \( 4s\sigma_g \) term value in \( CS_2 \) will be \( \approx 25\% \) larger than this. On this basis, the probable location of the \( \tau_g \rightarrow 4s\sigma_g \) transition in the \( CS_2 \) spectrum is between 1800 and 1900 Å. Two transitions occur in this region (see Fig. 5.1):

(i) The very intense \( \Lambda \) system which extends from 1850-2300 Å and which has been partially analysed by A.E. Douglas et al. as having a bent, \( ^1B_2 \), upper state.

(ii) A less intense diffuse transition at 1818 Å.

In Price's early paper on the vacuum u-v spectrum of \( CS_2 \) it was suggested that the absorption band at 1818 Å was due to a transition between non-bonding atomic orbitals
(possibly $3p \rightarrow 4s$). Unfortunately this statement is misleading because it implies that the transition is allowed by the atomic selection rule $\Delta l = \pm 1$. It is true that the highest occupied non-bonding $\pi_g^p$ Mo in CS$_2$, from which Price suggests the electron is excited, is composed largely of sulphur 3p orbitals, but in an atomic (united-atom) description the $\pi_g^p$ Mo becomes $nd\pi_g$.

\[ \pi_g^p \cong N(3p\pi - 3p\pi) \]
\[ \pi_g^p \cong nd\pi_g \]

Therefore the transition is $3d \rightarrow 4s$, not $3p \rightarrow 4s$, and is forbidden.

McGlynn et al.\textsuperscript{59} assign the 1818 Å transition in CS$_2$ to $\pi_g \rightarrow 4s\pi_g$ but there are certain ambiguities in their discussion of the transition. Thus, in the text of McGlynn's paper it is stated that the 1818 Å band is "weak but very wide in agreement with the forbidden nature of the $\pi_g \rightarrow n\sigma_g$ series". However, the same paper includes tables of estimated oscillator strengths for CS$_2$ Rydberg transitions which show that the 1818 Å band is in fact one of the strongest CS$_2$ absorptions in the region 1900–1200 Å and is certainly more intense than CS$_2$ bands described elsewhere by McGlynn\textsuperscript{59} as being "very strong".
It is clear from this discussion that misleading statements have been made by both Price and McGlynn concerning the 1818 Å transition in CS$_2$ and a clarification of the assignment of the transition is required. Because the model potential calculations of the present work locate the $\pi_g \rightarrow 4s\sigma_g$ transition in CS$_2$ between 1800 and 1900 Å, two assignments of the transitions in this region of the CS$_2$ spectrum appear to be possible:

(A) The 1818 Å transition is due to,

$$(\pi_g)^3 4s\sigma_g \frac{1}{2} \pi_g \rightarrow (\pi_g)^4 1\Sigma_g^+,$$

and the intense $\tilde{A}$ system is, as Walsh has proposed,

$$1B_2 + (\pi_g)^4 1\Sigma_g^+,$$

where the 1$B_2$ state is derived from the sub-Rydberg, $(\pi_g)^3 \pi_u 1\Sigma_u^+$ state in a bent conformation.

(B) The $\tilde{A}$ system is due to the Rydberg transitions,

$$(a_2)^2 b_2 \{ 4s\sigma_1 \} 1B_2 \rightarrow (\pi_g)^4 1\Sigma_g^+$$

where the $4s\sigma_1$ and $4p\sigma_1$ Mo's are derived from $4s\pi_g$ and $4p\pi_u$ Mo's in a bent conformation. In this case the 1818 Å transition may arise from the excitation of a bonding $\pi_u$ electron to a Rydberg orbital i.e.,

$$(\pi_u)^3 (\pi_g)^4 4s\sigma_g \frac{1}{2} \pi_u \rightarrow (\pi_u)^4 (\pi_g)^4 1\Sigma_g^+.$$


which is an allowed transition.

Neither assignments (A) or (B) is completely satisfactory but if assignment (B) is correct, the 1818 Å band is the first member of a \( \pi_u + n\sigma_g \) series converging to the \( 2\pi_u \) limit of \( \text{CS}_2 \), identified by M. Ogawa et al.\textsuperscript{74} and the \( 4\sigma_g \) term value is exceptionally high. Furthermore a comparison with the \( \text{CSe}_2 \) spectrum (see Chapter 6) shows that the analogue of the \( \text{CS}_2 \) 1818 Å transition in \( \text{CSe}_2 \) is very weak and certainly corresponds to a forbidden transition. For this reason we shall follow McGlynn\textsuperscript{59} in assuming the 1818 Å band in \( \text{CS}_2 \) is due to a \( \pi_g \rightarrow 4\sigma_g \) transition and assignment \( \Lambda \) is correct. The most unsatisfactory aspect of such an assignment is that a \( \pi_g \rightarrow 4\sigma_g \) transition is forbidden by the \( g \rightarrow g \) selection rule which is applicable to linear symmetric molecules; alternatively, if the upper state is bent and/or unsymmetrical the transition is allowed but should then show extended vibrational structure. Thus if assignment (A) is correct the high intensity and band profile of the 1818 Å transition are anomalous.

(ii) \( 4p\pi_u \) and \( 4p\sigma_u \)

The calculated term values for the \( 4p\pi_u \) and \( 4p\sigma_u \) levels of \( \text{CS}_2 \) are 0.0847 and 0.0865 a.u. respectively, although comparison with the \( \text{CO}_2 \) calculation shows that the observed \( np\pi \rightarrow np\sigma \) splitting in \( \text{CS}_2 \) is probably larger than the calculated value of \( \approx 0.003 \) a.u.
A very strong transition is observed in the CS$_2$ spectrum at 1595 Å with a term value of 0.0857 a.u. This transition is accompanied by a much weaker band at 1612 Å (see fig. 5.I). In view of the similarity of the 1595 Å transition to the 1088 Å band in CO$_2^+$ which was assigned to $\pi_g \rightarrow 3\sigma_u$ in this thesis, the following assignments of these CS$_2$ bands have been made:

1595 Å Band $\pi_g \rightarrow 4\sigma_u (^1\Pi_u)$

1612 Å Band $\pi_g \rightarrow 4\sigma_u (^3\Pi_u)$

Transitions to the triplet state are weakly allowed due to tendencies away from $(\Lambda, S)$ coupling and towards $(\Pi_C, \omega)$ coupling in CS$_2$ Rydberg states.

This assignment is in partial agreement with McGlynn$^{59}$ and Hasted$^{72}$. Thus both of these authors assign the CS$_2$ 1595 Å band to $\pi_g \rightarrow 4\pi_u$; McGlynn$^{59}$ does not state whether the Rydberg orbital is $4\sigma_u$ or $4\pi_u$ while Hasted$^{72}$ proposes $4\pi_u$. The 1612 Å band apparently does not show up in Hasted's$^{72}$ electron energy-loss spectra of CS$_2$ and we have already demonstrated (p. 128) that McGlynn's$^{59}$ assignment of the 1612 Å band to $\pi_g \rightarrow 3d_c$ is unacceptable. We shall now present spectroscopic evidence for the assignment of the 1595, 1612 Å bands to $\pi_g \rightarrow 4\pi_u (^1\Pi_u, ^3\Pi_u)$, rather than $\pi_g \rightarrow 4\pi_u$:

(i) In $(\Pi_C, \omega)$ coupling the interval $E(^1\Pi_u - ^3\Pi_u)$ should be similar to, but larger than, the spin-orbit coupling constant, $\lambda$, for CS$_2^+$. This is found to be the case because $\lambda = 436$ cm$^{-1}$
and \( E(1\Pi_u - 3\Pi_u) = 675 \text{ cm}^{-1} \). This value for \( E(1\Pi_u - 3\Pi_u) \) was obtained by E. Finn using high resolution photographs of the \( \text{CS}_2 \) spectrum taken on a 21 ft. off-plane Eagle mounted vacuum spectrograph.

(ii) The high resolution photographs, mentioned in (i) above, show that the 1595 \( \AA \) band has three heads corresponding to the \( P, Q \) and \( R \) branches expected for a \( \Pi - \Sigma \) transition.

Turning our attention to the \( \pi_g \rightarrow 4p\pi_u \) transition in \( \text{CS}_2 \), we have shown (p. 102) that for the analogous transition in \( \text{CO}_2 \) the upper state is probably bent. It is therefore likely that the upper state is also bent for \( \pi_g \rightarrow 4p\pi_u \) in \( \text{CS}_2 \) and the absorption due to this transition should show progressions in quanta of the bending vibration, \( \nu_2 \). The model potential calculations indicate that \( \pi_g \rightarrow 4p\pi_u \) should be observed in the \( \text{CS}_2 \) spectrum between the \( \pi_g \rightarrow 4p\pi_u \) and \( \tau_g \rightarrow 4s\sigma_g \) transitions, but the only observed transition in this region is the very weak system \( \sim 1720 \text{ \AA} \). McGlynn has suggested that this system consists of a progression in two quanta of the bending vibration in which case the upper state may be \((\pi_g)^3 4p\pi_u, 1\Sigma_u^+\), correlating with \( 1\Pi_2 \) in a bent conformation.

It is interesting that the assignment proposed here of the \( \tau_g \rightarrow 4p\sigma_u \) and \( 4p\pi_u \) transitions to the 1595 and 1720 \( \AA \) systems of \( \text{CS}_2 \) is the reverse of that suggested by Hasted, but, as we have already pointed out, the latter author gave no justification for the ordering of \( \pi \) terms he selected.
The Higher Members of the $\pi_g + n\lambda$ Rydberg series of $\text{CS}_2$

(i) $n\sigma_g$ and $n\delta_g$ series

The model potential calculation predicts that the transition $\pi_g + 5\sigma_g$ should be observed at 1406 Å (71100 cm$^{-1}$) in the $\text{CS}_2$ spectrum. On the other hand, the quantum defect for the observed $\pi_g + 4\sigma_g$ transition places the $\pi_g + 5\sigma_g$ transition at 1435 Å (69700 cm$^{-1}$). Transitions to a non-penetrating $3\delta_g$ level should be observed at 1440 Å while transitions to a penetrating $3\pi_g$ or $3\delta_g$ orbital will be to the red of this.

Inspection of the $\text{CS}_2$ spectrum shows that a strong transition occurs at 1410 Å, the strongest band in the 1420 Å group listed by Tanaka et al. This band is assigned to the transition $\pi_g + 5\sigma_g$, although McGlynn assigns it to $\pi_g + 4\pi_u$, i.e., the first member of an $np\pi_u$ series. McGlynn's assignment is not followed because the 1410 Å band has an unacceptable quantum defect for an $np$ term.

The absorption bands at 1500 Å are assigned to members of $a \pi_g + 3\delta_g$ complex, while the bands at 1440 Å probably belong to $a \pi_g + 3\pi_g$ transition.

On the basis of the quantum defects of $\text{CS}_2$ transitions already assigned to $\pi_g + n\sigma_g$ and $n\delta_g$, the $\pi_g + 4\delta_g$ and $6\sigma_g$ transitions should lie between 1320 and 1340 Å in the $\text{CS}_2$ spectrum. These transitions are very close to the $\pi_g + 6\pi_u$ and $\pi_g + 4\pi_u$ transitions and it is also possible that the
allowed transition \( \pi_u \rightarrow 4s_\sigma \) occurs in this region of the
\( \text{CS}_2 \) spectrum. Because the \( \text{CS}_2 \) spectrum below 1350 \( \AA \) is
very complex and high resolution spectra of this region were
not available we have not made detailed assignments of \( ns_\sigma \)
and \( nd_\lambda \) terms below 1400 \( \AA \). Instead, we shall consider the
\( \text{CS}_2 \) Rydberg series that have been well established in this
region of the spectrum, viz Price's \(^{70}\) series I and II. These
series are assigned to \( \pi \rightarrow np\lambda_u \) for reasons discussed in the
next sub-section.

(ii) \( np\sigma_u \) and \( np\pi_u \) series

The calculated values for the \( 5p\lambda_u \) terms of \( \text{CS}_2 \) predict
that the \( \pi \rightarrow 5p\lambda_u \) transitions should be observed at 1380 \( \AA \)
\((72460 \text{ cm}^{-1})\) in the \( \text{CS}_2 \) spectrum, with the \( 5p\pi \) level to the
red of the \( 5p\sigma \) level. There is a complex absorption system
in this region of the spectrum referred to by Tanaka et al.
as the 1385 \( \AA \) group. Two bands at 1369 \( \AA \) and 1378 \( \AA \) constitute
members of Price's \(^{70}\) Rydberg series I and II. The 1385 \( \AA \)
group is assigned to transitions belonging to a \( \pi \rightarrow 5p\lambda_u \)
complex in which the \( 5p\pi_u \) components are much weaker than the
\( 5p\lambda_u \) components in analogy to the \( \pi \rightarrow 4p\lambda_u \) transitions in \( \text{CS}_2 \).
Price's \(^{70}\) series I and II are listed in table 5.11
together with calculated \( np\sigma_u \) and \( np\pi_u \) term values. Because
the \( \pi \rightarrow np\pi_u \) series appears to be very weak in \( \text{CS}_2 \) the series
I and II are assigned to the singlet and triplet components of
the \( \pi_u \) states derived from the excited state configuration
\((\pi_u)^3 \) \( np\sigma_u \).
Hasted et al.\textsuperscript{72} have suggested that Price's\textsuperscript{70} series I and II constitute "vibrationally excited and unexcited versions of the same series"; this is possible but does not account for the fact that the strongest Rydberg series converging to the lowest I.P. in CO\textsubscript{2}, CS\textsubscript{2} and CSe\textsubscript{2} all consist of two components split by an interval which approaches the spin-orbit splitting in the respective ion. In CS\textsubscript{2} this splitting is similar to $v_2$ but comparison with CO\textsubscript{2} and CSe\textsubscript{2} shows that Price's\textsuperscript{70} series I and II in CS\textsubscript{2} are as assigned in this thesis i.e. singlet and triplet components of the same series occurring with similar intensity in ($\Omega_C, \omega$) coupling.

The only intense CS\textsubscript{2} absorption above 1325 Å that has not been assigned in this thesis is located at 1342 Å. The term value of this transition is very close to a non-penetrating $4f\lambda_u$ term and the transition is therefore assigned to the first member of the $\pi_g - n\lambda_u$ series in CS\textsubscript{2}.

A summary of the CS\textsubscript{2} Rydberg assignments made in this thesis compared with those made previously by McGlynn\textsuperscript{59} and Hasted\textsuperscript{72} is given in table 5.III. A diagram showing the complete CS\textsubscript{2} assignments of the present work is given in Fig. 5.I.
Fig. 5.1

CS$_2$ Spectrum from 1300-1900 Å Showing $\sigma_g - n\pi^*$ Assignments
Table 5.I

Calculated Terms for $\text{CS}_2$

<table>
<thead>
<tr>
<th>n</th>
<th>$n \sigma^g$ (a.u.)</th>
<th>$n \sigma^u$ (a.u.)</th>
<th>$n \pi^u$ (a.u.)</th>
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<td>.0417</td>
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<td>.0237</td>
<td>.0245</td>
</tr>
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<td>.0176</td>
<td>.0157</td>
<td>.0161</td>
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<tr>
<td>6</td>
<td>.0123</td>
<td>.0112</td>
<td>.0114</td>
</tr>
<tr>
<td>7</td>
<td>.0091</td>
<td>.0084</td>
<td>.0085</td>
</tr>
</tbody>
</table>

Table 5.II

Price's Series I and II for $\text{CS}_2$ Compared to Calculated $n \pi^u$ Series

<table>
<thead>
<tr>
<th>n</th>
<th>Series I</th>
<th>Series II</th>
<th>$n \sigma^u$</th>
<th>$n \pi^u$</th>
</tr>
</thead>
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<td>.0876</td>
<td>.0847</td>
<td>.0865</td>
</tr>
<tr>
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<td>.0243</td>
<td>.0237</td>
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<tr>
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<td>.0161</td>
</tr>
<tr>
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<td>7</td>
<td>.0088</td>
<td>.0088</td>
<td>.0084</td>
<td>.0085</td>
</tr>
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</table>
Table 5.III
Assignments of the CS₂ Spectrum in the Region 1325-1825 Å

<table>
<thead>
<tr>
<th>CS₂ Absorption Å</th>
<th>Previous Assignments</th>
<th>Present Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>1818 g_π→4sσ</td>
<td>g_π→4sσ</td>
<td>g_π→4sσ, 1_π</td>
</tr>
<tr>
<td>1720 g_1Σ→1Π (Bent)</td>
<td>g_π→4pσ</td>
<td>g_π→4pσ, (4pa_1B₂)</td>
</tr>
<tr>
<td>1612 g_π→3dλ</td>
<td>g_π→3dλ</td>
<td>g_π→3dλ, 3_π</td>
</tr>
<tr>
<td>1595 g_π→4pλ</td>
<td>g_π→4pλ</td>
<td>g_π→4pλ, 1_π</td>
</tr>
<tr>
<td>1475-1525 g_2σ→1,3_Π</td>
<td>g_2σ→1,3_Π</td>
<td>g_2σ→1,3_Π</td>
</tr>
<tr>
<td>1440 g_π→5sσ</td>
<td>g_π→5sσ</td>
<td>g_π→3dσ, 1_π and 3_π</td>
</tr>
<tr>
<td>1410 g_π→4pλ</td>
<td>g_π→4pλ</td>
<td>g_π→5sσ, 1_π</td>
</tr>
<tr>
<td>1378 g_π→4dλ</td>
<td>g_π→4dλ</td>
<td>g_π→5pσ, 3_π</td>
</tr>
<tr>
<td>1369 g_π→5pλ</td>
<td>g_π→5pλ</td>
<td>g_π→5pσ, 1_π</td>
</tr>
<tr>
<td>1342 g_π→5sλ</td>
<td>g_π→5sλ</td>
<td>g_π→4fσ, 1_π</td>
</tr>
</tbody>
</table>

First members of Price's series

S.P. McGlynn et al.⁵⁹ J.B. Hasted et al.⁷²
CHAPTER 6

RYDBERG SERIES IN CSe₂

6.1 Previous Work

In this thesis the vacuum u-v spectra of CO₂ and CS₂ have been analysed using model potential calculations of their Rydberg series. CSe₂ is the next member of this group of 16 valence-electron linear triatomic molecules and model potential calculations were carried out on CSe₂ for the determination of its Rydberg series.

The u-v spectrum of CSe₂ has been investigated by G.W. King and K. Srikameswaran. Up to the present time, no spectra of CSe₂ below 2000 Å have been reported in the literature; the Rydberg series of CSe₂ certainly lie in this region of the spectrum and for this reason CSe₂ was synthesised and vacuum u-v spectra of the gas were obtained.

Synthesis of CSe₂

CSe₂ was synthesised by the method used by K. Srikameswaran and which is a modified version of the procedure first reported by D.J.G. Ives et al. Metallic selenium is heated with methylene chloride, (in milligram quantities), to 600°C when the golden yellow gas CSe₂ forms in >50% yield. The balanced equation for this reaction is:

\[
600°C \quad CH₂Cl₂ + 2Se \rightarrow CSe₂ + 2HCl
\]
The reaction tube contains, after cooling, CSe$_2$ and HCl as well as unreacted CH$_2$Cl$_2$. The effect of these impurities on the CSe$_2$ spectrum will be discussed in a later section.

6.2 The vacuum u-v spectrum of CSe$_2$

A. Experimental

The vacuum u-v spectrum of CSe$_2$ in the region 1200-2000 Å was obtained using a McPherson Model 225 1-metre scanning monochromometer. A McPherson Model 630 lamp producing a low pressure (~2 mm) discharge in hydrogen at 2000 V and 350 mA was used as the source of vacuum u-v radiation. This discharge lamp provides a good continuum from 2000-1675 Å but below these wavelengths the continuum is overlayed by the hydrogen "many-line" spectrum which extends down to the H α-line at 1215 Å. To eliminate superposition of the source spectrum on the sample spectrum, double-beam operation was used with two matched E.M.I. Type 9635 B photomultipliers and a Burr-Brown Model 1665/16 log ratio amplifier as the detection system. Photomultiplier dark currents were backed-off by applying a variable, reverse D.C., voltage to the photomultiplier outputs, and source "following" in the sample spectrum was checked for by recording the spectrum of the discharge lamp simultaneously with the sample spectrum.

Absorption spectra of CSe$_2$ were obtained by introducing gas samples into a 10 cm cell, (with LiF windows), that had been previously evacuated to at least 0.002 mm Hg.

B. The effect of Impurities

The vacuum u-v spectrum of CSe$_2$ was first obtained using
gas samples taken directly from the reaction tube used in the synthesis; the samples therefore consisted of a mixture of CSe₂, CH₂Cl₂ and HCl. With sample pressures \( \approx 0.25 \) mm Hg many intense absorption features were obtained in the vacuum u-v spectrum from 1250-2000 Å. To discover which of these features were due to absorption by CSe₂ and which were caused by the other gases in the sample, the vacuum u-v spectra of HCl and CH₂Cl₂ were obtained separately.

At a pressure of 1 mm Hg, the HCl spectrum showed a very weak continuous absorption from 1800-1400 Å together with stronger discrete features at 1331, 1290 and 1283 Å. These discrete features were apparent in the CSe₂ spectra obtained using gas samples directly from the CSe₂ synthesis, and a procedure for removing HCl from the CSe₂ samples was therefore devised. The CSe₂ sample was passed over Mg ribbon at room temperature and the H₂ gas formed was pumped off the sample at liquid N₂ temperatures. In this way the strong HCl absorptions at 1331, 1290 and 1283 Å were eliminated from the CSe₂ spectrum as shown in Fig. 6.1.

At a pressure of 0.2 mm Hg the spectrum of CH₂Cl₂ shows a region of continuous absorption extending from 1700-1450 Å with \( \lambda_{\text{max}} \approx 1510 \) Å. To shorter wavelengths a strong continuum is observed from 1400-1340 Å overlaid by several discrete bands, the wavelengths of which have been published by A.B.F. Duncan et al. Comparison of the CSe₂ spectrum obtained from
Effect of HCl and CH₂Cl₂ Impurities on CSe₂ Spectrum

A CSe₂ Spectrum before HCl removed
B CSe₂ Spectrum after HCl removed

CH₂Cl₂ Absorption Bands
the CSe₂ sample containing unreacted CH₂Cl₂, showed that
the CH₂Cl₂ bands are of much lower intensity than the CSe₂ bands, (See Fig.6.1 ). Consequently no attempt was made
to remove CH₂Cl₂ from CSe₂ samples because the presence of
this impurity does not interfere with the analysis of the
spectrum.

While the expected impurities, HCl and CH₂Cl₂, did
not seriously obscure the CSe₂ spectrum, CS₂ appeared as an
unexpected impurity, in the first CSe₂ samples prepared, and
obscured parts of the CSe₂ spectrum; this impurity was
identified by the presence of discrete bands in the region
1850-2150 Å whose wavelengths fitted the published data on
the Å system of CS₂ 54,73. The first samples of CSe₂ used for
obtaining spectra were prepared from high purity CH₂Cl₂, (Baker
"Instra Analysed" Spectrophotometric grade), and Analar Selenium,
(B.D.H. Ltd.). However, the CS₂ Å system showed up with the
same intensity in the vacuum u-v spectrum as the strongest CSe₂
bands. In later samples, ultra high purity (99.9997%) selenium
was used, (Chemicals Procurement Labs); while the CS₂ Å system
was still not completely eliminated from the CSe₂ spectrum,
a new system of bands was observed in the same region and was
assumed to belong to CSe₂.

6.3 Model Potential Calculations of the Rydberg Series of CSe₂

The model potential calculation developed in this thesis
was applied to CSe₂ to estimate the term values for the
\( \pi_g + n\sigma_g \), \( n\sigma_u \), and \( np\pi_u \) Rydberg series. The calculated
values are given in Table 6.1 in a.u.'s.

Table 6.1
Calculated Terms for CSe₂

<table>
<thead>
<tr>
<th>n</th>
<th>ns(\sigma_g) (a.u.)</th>
<th>np(\sigma_u) (a.u.)</th>
<th>np(\pi_u) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1060</td>
<td>0.0847</td>
<td>0.0867</td>
</tr>
<tr>
<td>3</td>
<td>0.0487</td>
<td>0.0404</td>
<td>0.0417</td>
</tr>
<tr>
<td>4</td>
<td>0.0279</td>
<td>0.0239</td>
<td>0.0245</td>
</tr>
<tr>
<td>5</td>
<td>0.0180</td>
<td>0.0158</td>
<td>0.0161</td>
</tr>
<tr>
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<td>0.0126</td>
<td>0.0112</td>
<td>0.0114</td>
</tr>
<tr>
<td>7</td>
<td>0.0093</td>
<td>0.0084</td>
<td>0.0085</td>
</tr>
</tbody>
</table>

The most striking feature of the calculated term
values for CSe₂ is their close agreement with the calculated
values for CS₂, given in Table 5.1. This suggests that the
analysis of the CSe₂ Rydberg spectrum should follow closely
the analysis already proposed for CS₂. The first ionisation
potential of selenium is \( \sim 0.61 \) ev lower than the first ionisation
potential of sulphur; for this reason the CSe₂ spectrum should
resemble the CS₂ spectrum, but shifted \( \sim 4900 \text{ cm}^{-1} \) to the red.
Also, the spin-orbit coupling in selenium is much larger than
that in sulphur, and all the Rydberg states of CSe₂ are probably
well described by \( (\Omega, \omega) \) coupling. Consequently, singlet-triplet
intensity ratios should be much closer to unity than those
observed in CS₂.
In going from CO$_2$ to CS$_2$ the relative intensity of the $\pi^+_g \to \pi^-_u$ series diminished considerably. This trend should be continued in going from CS$_2$ to CSe$_2$ and the series $\pi^+_g \to \pi^-_u$ may not be observed in the CSe$_2$ spectrum.

6.4 Analysis of the CSe$_2$ Vacuum u-v Spectrum

The results of the model potential calculations on CS$_2$ and CSe$_2$ indicate that the observed CS$_2$ term values should be very close to the observed CSe$_2$ terms. The term value of a Rydberg state, $\psi(n\ell\lambda)$, can be used to locate the transitions $\pi^+_g \to n\ell\lambda$ in the spectrum only if the ionisation potential or the limit to which the Rydberg series converge, is known. The first ionisation potential of CSe$_2$ is unknown but is probably close to $81300 \pm 4900$ cm$^{-1}$ or $\approx 76,000$ cm$^{-1}$. An accurate value for the first ionisation potential of CSe$_2$ can be obtained from the identification of Rydberg series in the vacuum u-v spectrum of the molecule; these series will lie at lower excitation energies than 76,000 cm$^{-1}$ or to the red of 1300 Å.

(i) Rydberg series in the 1300-1500 Å region of the CSe$_2$ spectrum

Two intense Rydberg series were identified in the CSe$_2$ spectrum in the region 1300-1500 Å, with limits at 74665 ± 15 cm$^{-1}$ and 76785 ± 25 cm$^{-1}$. These will be designated series I and II respectively, and fit the formulae:

CSe$_2$ Series I

$$v_n = 74665 - \frac{R}{(n - 0.11)^2}$$

n = 4, 5, ... 9
CSe₂ Series II

\[ \nu_n = \frac{76785 - \frac{R}{(n - 0.12)^2}}{n=4,5...10} \]

The observed bands belonging to these series are given in table 6.1I together with their intensities (Relative to I = 10.0 for the CSe₂ transition at 1735.5 Å). Also in the table, the observed frequencies, \( \nu_{\text{obs}} \), are compared with values, \( \nu_{\text{calc}} \), determined from the Rydberg formulae.

The Rydberg series I and II in CSe₂ give the lowest ionisation potential of CSe₂ as 9.257 ± 0.002 ev and the spin-orbit coupling constant, \( \Lambda \), for the ion CSe₂⁺ as 2120 ± 30 cm⁻¹.

The small quantum defects found for series I and II, and the fact that the series terminate at \( n=4 \), suggests that they constitute \( ^1, ^3 \Pi \) components (\( \Omega = 1 \)) of the \( \pi_g + n\lambda_u \) Rydberg series of CSe₂ with \( \lambda_u \) either \( \sigma_u \) or \( \delta_u \). This assignment brings out the predicted similarity of CSe₂ terms with the equivalent terms in CS₂. Thus the average term value for the lowest members of series I and II in CSe₂ is 7270 ± 20 cm⁻¹. In the CS₂ spectrum the band at 1342 Å was assigned (see p.137) to the first member of the \( 1\pi_g \rightarrow n\sigma_u \) series in CS₂ and has a term value of 7240 ± 20 cm⁻¹.

(iii) The Assignment of \( ns_g, np_u \) and \( nd_g \) terms in the CSe₂ Spectrum

Knowing the ionisation potential of CSe₂, the assignment of \( ns_g, np_u \) and \( nd_g \) series in CSe₂ can be made by direct
Table 6.11
Principal Rydberg Series of CSe$_2$ in the Region 1300-1500 $\AA$

CSe$_2$ Series I

<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda_{obs}$ (Å)</th>
<th>I$_{rel}$</th>
<th>$\nu_{obs}$ (cm$^{-1}$)</th>
<th>$\nu_{calc}$ (cm$^{-1}$)</th>
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<td>73275</td>
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<td>10</td>
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<td>-</td>
<td>-</td>
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<td>$\lambda$'s to ± 0.5 $\AA$</td>
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<td>74665</td>
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CSe$_2$ Series II

<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda_{obs}$ (Å)</th>
<th>I$_{rel}$</th>
<th>$\nu_{obs}$ (cm$^{-1}$)</th>
<th>$\nu_{calc}$ (cm$^{-1}$)</th>
</tr>
</thead>
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<td>0.9</td>
<td>75670</td>
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</table>
comparison with appropriate term values in CS₂.

\[ \pi_g + 5s\sigma_g \]

From the observed 4s\(s\) term value in CS₂, the \(\pi_g + 5s\sigma_g\) excitation energy in CSe₂ can be estimated to be 50100±200 cm\(^{-1}\) for the singlet-singlet transition and 48000±200 cm\(^{-1}\) for the singlet-triplet transition. This places \(\pi_g + 5s\sigma_g (\Pi_g^1)\) and \(\pi_g + 5s\sigma_g (\Pi_g^3)\) at 1995 and 2085±10 Å respectively. The CSe₂ spectrum in this region shows a weak system extending from 1975 to 2125 Å, with \(\lambda_{\text{Max}}\) γ 2040 Å. This system is certainly due to \(\pi_g + 5s\sigma_g\). However, the absorption bands are partially obscured by the Å system of CS₂ which occurred as an impurity in the CSe₂ samples (see p.145), and no assignment of singlet and triplet components will be made.

\[ \pi_g + 5p\sigma_u \]

The observed 4p\(\sigma_u\) term value in CS₂ is 19150±50 cm\(^{-1}\) and the same value for the lowest np\(\sigma_u\) term in CSe₂ would place the \(\pi_g + 5p\sigma_u\) transition at 1802±5 Å (triplet component) and 1738±5 Å (singlet component) in the CSe₂ spectrum. Two very strong transitions are found in the CSe₂ spectrum very close to these values, one at 1735.5 Å and the other, a weaker doublet, at 1802 Å; these are undoubtedly \(1\Pi(1) + 1\Sigma^+\) and \(3\Pi(1) - 1\Sigma^+\) respectively. The intensity ratio, \(I(\Pi) / I(\Sigma) = 0.5\), is consistent with \((\pi_C, \omega)\) coupled states; the tendency away from \((\pi, S)\) and towards \((\pi_C, \omega)\) coupling in going from CS₂ to CSe₂ is readily apparent by comparing the first member of the
π₉ + np₉u series in each molecule (See Fig. 5.1 and Fig. 6.2).

The energy interval E(1π - 3π) for π₉ + 5π₉u in CSe₂ equals 2125±10 cm⁻¹ and is close to the A value of 2120±30 cm⁻¹ found for CSe²⁺; this is also expected for states which are close to ideal (ΩC,ω) coupling. (See diagram p.87)

π₉ + 4dλ₉ and higher g ↔ g transitions

Transitions belonging to the π₉ + 4dλ₉ complex in CSe₂ should occur in the vacuum u-v spectrum between 1525 and 1700 Å. Numerous transitions are observed in this region but they are all weak and diffuse; the strongest occur at 1545 Å and are probably part of a π₉ + 4dδ₉ transition.

It appears that g ↔ g transitions are weak in the CSe₂ spectrum and higher members of π₉ + nλ₉ series are certainly obscured by stronger g ↔ u series.

The higher members of the π₉ + np₉u series of CSe₂

In the discussion of the CS₂ Rydberg spectrum, Price's series I and II were assigned to 1π₉ + np₉u, 1,3π₉u. In addition the CS₂ transitions at 1595 and 1612 Å were assumed to constitute the first members of Price's series, implying that the quantum defects for these series are 1.44 and 1.46.

In view of the similarity of the CS₂ and CSe₂ term values, CSe₂ should exhibit similar π₉ + np₉u series to CS₂ but with a quantum defect ~2.45. Two series, designated III and IV were found in the CSe₂ spectrum with quantum defects close to this value and are assigned to π₉ + np₉u, 1,3π₉u by analogy with CS₂.
These series fit the formulae:

\[
CSe_2 \text{ Series III} \\
\frac{n}{n - 2.45}^2 = 74665 - \frac{R}{(n - 2.45)^2} \\
n = 5, 6, \ldots 10
\]

\[
CSe_2 \text{ Series IV} \\
\frac{n}{n - 2.46}^2 = 76785 - \frac{R}{(n - 2.46)^2} \\
n = 5, 6, \ldots 10
\]

(See table 6.III)

The occurrence of series III and IV in the CSe₂ spectrum again emphasises the similarity of the CSe₂ and CS₂ Rydberg spectra. Perhaps the most significant difference between the spectra of the two molecules is the increased intensity of \( \pi_g - nf \sigma_u \) series relative to \( \pi_g - np \sigma_u \) in CSe₂ compared to CS₂.

The only CSe₂ bands, with significant intensity in the vacuum u-v between 2000 and 1200 Å, that are unassigned in this thesis occur at 1511, 1465, 1448 and 1413 Å. It is probable that these transitions are other \( \Omega = 1 \) components of the \( \pi_g - nf \sigma_u \) series in addition to those already assigned to series I and II, or alternatively they may constitute the first members of \( \pi_u - ni \) series in CSe₂.

A diagram showing the assignments of CSe₂ absorptions between 1325 and 1525 Å proposed in this thesis are given in Figs. 6.II and 6.III.
Table 6.3II

Additional Rydberg Series of CSe₂ in the
Region 1300-1900 Å

CSe₂ Series III

<table>
<thead>
<tr>
<th>n</th>
<th>( \lambda_{\text{obs}} ) (Å)</th>
<th>( I_{\text{rel}} )</th>
<th>( \nu_{\text{obs}} ) (cm(^{-1}))</th>
<th>( \nu_{\text{calc}} ) (cm(^{-1}))</th>
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<td>57795</td>
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</tr>
<tr>
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<td>72125</td>
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\( \lambda = 0.5 \) Å

CSe₂ Series IV

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<th>n</th>
<th>( \lambda_{\text{obs}} ) (Å)</th>
<th>( I_{\text{rel}} )</th>
<th>( \nu_{\text{obs}} ) (cm(^{-1}))</th>
<th>( \nu_{\text{calc}} ) (cm(^{-1}))</th>
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</tbody>
</table>

\( ^1 \) Superimposed with another band
Fig. 6.11

CS₂ Spectrum from 1700-2000 Å Showing π g → nπ l Assignments

Series III

Series IV

Wavelength (Å)
Fig. 6.11

CS\(_2\) Spectrum from 1300-1600 Å Showing \( v_g \): \( n\ell \) Assignments

- Series I: \( n\ell \sigma_u \), \( ^3\Pi_u \)
- Series II: \( n\ell \sigma_u \), \( ^1\Pi_u \)
- Series III: \( n\sigma_u \), \( ^3\Pi_u \)
- Series IV: \( n\sigma_u \), \( ^1\Pi_u \)

Wavelength (Å)
CONCLUSIONS

"Don't suppose that you can tell it precisely the first dozen times you try, but at 'em again... Not that the story need be long, but it will take a long time to make it short."

H.D. Thoreau

In this thesis a theoretical method was developed for the calculation of Rydberg series in triatomic molecules. The method is an extension of that proposed by S.A. Rice et al. and involves the determination of parameters which establish atomic model potentials for use in molecular calculations. A new parametrisation procedure was used in the present work which optimises not only the energy eigenvalue but also the asymptotic phase-shift of the model Rydberg A.O.

We suggest that further work on atomic model potentials should be aimed at finding connecting formulae between the quantum defect and model potential parameters.

The first one-centre calculations of Rydberg series in CO$_2$, CS$_2$, and CSe$_2$ were carried out in Chapter 2 of this thesis, and an estimate of the $l$-purity of Rydberg states in these molecules was made by comparison with H$_2^+$ wavefunctions. The conclusion that the $l$-purity is very high even in the lowest Rydberg states was confirmed by two-centre calculations of ns Rydberg series in CO$_2$: these calculations demonstrated the
united-atom (single-centre) character of CO$_2$ Rydberg MO's.

The CO$_2$ and CS$_2$ $\pi^g \rightarrow n\sigma_g$, n$\pi^g_u$ and n$\pi^u_u$ Rydberg series were determined using the model calculations and compared with the Rydberg series assigned by previous investigators; their assignments were shown to be unacceptable in several cases and new assignments were proposed where necessary.

The previously unreported vacuum u-v spectrum of CSe$_2$ was obtained and analysed in terms of Rydberg series, determined from the model calculation. The CS$_2$ and CSe$_2$ calculations predicted that the Rydberg terms in these molecules should be very similar and this was confirmed in the course of the analysis proposed for CSe$_2$.

The main difference between observed and calculated Rydberg terms in CO$_2$, CS$_2$ and CSe$_2$ was accounted for by the neglect of bonding effects in the core of the molecular model potential employed in the calculation. It was also suggested that smaller differences between calculated and observed Rydberg terms arose from changes in geometry in certain Rydberg excited state configurations; spectroscopic evidence was presented supporting proposed assignments of bent + linear transitions.
BIBLIOGRAPHY

2. N. Bohr, Phil. Mag. 26, 1 (1913).