# THEORY AND E.P.R. SPECTRA OF LINEAR FREE RADICALS

BY

Brian John Howard.

Bachelor of Arts at the University of Cambridge

A dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Southampton.

The University,
Highfield,
Southampton.

June 1970

I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the sea-shore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

Sir Isaac Newton:

Brewsters Memoirs of Newton, II.

ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Doctor of Philosophy

# THE THEORY AND E.P.R. SPECTRA OF LINEAR FREE RADICALS

by Brian John Howard.

This dissertation is concerned mainly with the theory needed to explain the gas-phase electron paramagnetic resonance spectra of linear free radicals.

The Hamiltonian operator describing the system is obtained by transforming the Pauli-Schrodinger form of the Breit equation from a space-fixed to a molecule-fixed axis system. From this an effective Hamiltonian, operating in just the ground vibronic state, is derived. This is then used to interpret the e.p.r. spectra of NS and CF. We obtain the electric dipole moment and information on the hyperfine parameters of these radicals.

The theory applicable to the energy levels of linear triatomic molecules is derived and the effects of the bending vibration on the e.p.r. spectra are obtained. Finally, the effects of case (c) coupling on the spectra of diatomic molecules are discussed; it is proposed that these are the cause of the discrepancies observed in the spectra of certain heavy molecules.

# ACKNOWLEDGEMENTS

I should like to take this oppotunity to thank my supervisor, Professor Alan Carrington, for his continual help and encouragement during the work for this thesis. I wish also to thank the other members of the Chemical Physics Group, especially Drs. Richard Moss and John Brown, for useful discussions and advice.

I should also like to express my gratitude to my wife for continual encouragement and patience during the writing of this thesis.

I thank the Science Research Council for financial assistance during the whole of this work.

# CONTENTS

Chapter 5 An Effective Hamiltonian and its Matrix Elements for a Linear Molecule

Chapter 6 The e.p.r. Spectrum of NS

Chapter 7 The E.p.r. Spectrum of CF

Chapter 8 The Renner Effect

# Chapter 1

# INTRODUCTION

The study of free radicals by the method of electron paramagnetic resonance started in the mid-1940's. Among the first radicals to be studied were the stable gases $O_2$[1] and NO[2], whose spectra have been analysed by many authors.[3-9].

Until quite recently, further work has been mainly restricted to liquids and solids. In the condensed phases, quantised rotational motion is completely quenched and we are consequently left with just the interaction of the electron spin with the applied magnetic field[10]. In the case of doublet states, the spectrum is approximately that of a free electron, centred on g=2, split by the hyperfine interaction with any magnetic nuclei present in the molecule. In solids, particularly single crystals, and also in liquid crystals it is possible to determine the anisotropy of the interactions, namely the g- and hyperfine tensors. In liquids the random tumbling motion averages all the anisotropic interactions. The spectrum then gives only the isotropic interaction parameters. The "rotational" motion only reveals itself in the linewidths; it is a possible mechanism for relaxation. In the case of molecules in triplet or higher multiplet states, or with appreciable orbital angular momentum, the spectrum may differ considerably from g=2, but we can always neglect rotation.

For gases at pressures of only a few torr, the rotational motion is quantised. In bent molecules (e.g. $NO_2$, $ClO_2$ and $NF_2$) the only interaction of the electron spin with the molecular framework is the spin-rotation coupling. The magnitude of this is typically a few hundred MHz, and at fields of the order of kilogauss this produces just a small perturbation on the basic $g=2$ spectrum. The same is true for linear paramagnetic species in $^2\Sigma$ electronic states. Other linear molecules show a strong interaction between the spin and the molecular framework. In doubly-degenerate electronic states, i.e. states with orbital angular momentum, the spin-orbit coupling interaction provides a strong coupling of the spin to the internuclear axis. In triplet and higher multiplet states, the spin-spin dipolar interaction provides a similar coupling; it is particularly important for molecules with heavy atoms because of their large second order spin-orbit effects. These interactions tend to modify the g-value and if the molecule is polar give some of the transitions tunable with a magnetic field electric dipole intensity. These transition intensities are about $10^4$ times greater than the magnetic dipole transitions observed in the condensed phases and in molecules with decoupled spin; consequently it is mainly radicals of this category that have been observed.

Following the work on the stable $O_2$ and NO, the unstable radicals OH [11], SH [12], SeH [13], TeH [13] and SO [14,15] have been observed;

the first four have a $^2\Pi$ and the last a $^3\Sigma$ ground state. Since then members of this laboratory have more than doubled the number of radicals. They have observed SO in its $^1\Delta$ [16] state as well as $^3\Sigma$ [17,18], SeO ($^3\Sigma$ and $^1\Delta$) [19], ClO [20], BrO [21], IO [21], SF [22], SeF [22], NS [23], and CF [24] (all in their $^2\Pi$ ground state). Recently the field has been enlarged by the detection of the linear triatomic radicals NCO and NCS (both with $^2\Pi$ ground electronic states) [25,26]. They show novel features, not previously observed, because of the interaction of the doubly degenerate vibration with the doubly degenerate electronic wavefunction. The theory of the resulting Renner interaction is described later in this work [27].

Most of these radicals have been previously observed by electronic spectroscopy where the rotational constant and the spin-orbit or the dipolar spin-spin coupling constant have been obtained. The e.p.r. spectra give these constants and in addition the magnetic hyperfine and electric quadrupole constants for magnetic nuclei, a measure of the rotational Zeeman interaction, small relativistic corrections to the electron spin and orbital g-factors, and in certain cases the spin-rotation interaction (in molecules which do not closely approximate to Hund's coupling case (a) ). Also by means of a Stark cavity developed in this group, it is possible to measure the dipole moment.

Recently pure microwave spectroscopy has been used to study unstable paramagnetic molecules. The microwave spectra yield accurate values of the rotational constant, together with the other non-Zeeman parameters (with comparable accuracy to e.p.r.). Also one can look at the essentially diamagnetic $^2\Pi_{\frac{1}{2}}$ state of radicals and obtain complementary data on the hyperfine interaction; it is then possible to seperate the various contributions, namely, the Fermi-contact term, the electron-nuclear spin-spin dipolar interaction and the orbit-spin interaction.

As yet pure microwave spectroscopy is confined to OH [28], SO [29], ClO [30], BrO [31], and NS [32] (all fairly long lived radicals) and appears to be less sensitive than e.p.r. . This is reasonable since it is easier to obtain a high concentration of short-lived radicals in the small resonant cavity of e.p.r. than in the long non-resonant wave-guide of a microwave spectrometer. Also the high 'Q' resonant cavity gives better signal-to-noise characteristics and hence greater sensitivity.

A great number of molecular constants are obtained from the electron resonance spectra and these can be used as sensitive tests of the accuracy of recent wavefunctions of open shell molecules. For example Carrington and Lucas compare the calculated and experimental hyperfine parameters of the isotopic forms of OH [33]. Another application of the techique of e.p.r. of gases is in kinetic studies. At present there is great interest in the radical intermediates in chemical reactions and quantitative determinations of their concentrations have been used in the study of the mechanism of several reactions (see for example Westenberg and de Haas [34]).

In this thesis, we start by first describing the experimental techniques for the study of radical spectra. Then in chapter 3, the theory for the interpretation of such spectra is derived as precisely as possible within the confines of relativistic quantum mechanics. Paramagnetic molecules contain many different kinds of angular momenta coupled together, and the evaluation of the matrix elements of the Hamiltonian is made far simpler by using irreducible spherical tensor techniques. The essential points of these Racah methods are discussed in chapter 4. Chapter 5 is concerned with calculating the energy levels. An effective Hamiltonian operating in only the ground vibronic state is derived and its matrix elements are evaluated. In chapters 6 and 7, we discuss the formation of NS and CF and the detailed analysis of their spectra. Chapter 8 is confined to the Renner effect. This is derived in a novel manner using degenerate perturbation theory. The important second and third order contributions have not been previously discussed but they have significant effects on the g-factor of the spectrum. In chapter 9, the effects of the spin-orbit coupling is described; this is believed to give the solution to the anomalies observed in the g-values of heavy radicals.

At certain points in the text it is necessary to obtain some fairly complicated mathematical results, and in order to preserve the logical developement of the theory, will be included in the appendices at the end of their respective chapters.

## References to Chapter 1

1. R. Beringer and J. G. Castle, Phys. Rev. 81, 82 (1951).
2. R. Beringer and J. G. Castle, Phys. Rev. 78, 581 (1950).
3. M. Tinkham and M. W. P. Strandberg, Phys. Rev. 97, 937,951 (1955).
4. K. D. Bowers, R. A. Kamper and C. D. Lustig, Proc. Roy. Soc. A251, 565 (1959).
5. J. M. Hendrie and P. Kusch, Phys. Rev. 107, 716 (1957).
6. R. Beringer, E. B. Rawson and A. F. Henry, Phys. Rev. 94, 343 (1954).
7. C. C. Lin and M. Mizushima, Phys. Rev. 100, 1726 (1955).
8. C. C. Lin, Phys. Rev. 119, 1027 (1960).
9. R. L. Brown and H. E. Radford, Phys. Rev. 147, 147 (1966).
10. For example, A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", (Harper & Row, New York, 1967).
11. H. E. Radford, Phys. Rev. 122, 114 (1960), ibid. 126, 1035 (1962).
12. H. E. Radford and M. Linzer, Phys. Rev. Lett. 10, 443 (1963).
13. H. E. Radford, J. Chem. Phys. 40, 2732 (1964).
14. C. C. McDonald, J. Chem. Phys. 39, 2587 (1963).
15. J. M. Daniels and P. B. Dorain, J. Chem. Phys. 40, 1160 (1964).
16. A. Carrington, D. H. Levy and T. A. Miller, Proc. Roy. Soc. A293, 108 (1966).
17. A. Carrington, D. H. Levy and T. A. Miller Proc. Roy. Soc. A298, 340 (1967).
18. A. Carrington, D. H. Levy and T. A. Miller, Mol. Phys. 13, 401 (1967).

19. A. Carrington, G. N. Currie, D. H. Levy and T. A. Miller,
to be published.

20. A. Carrington, P. N. Dyer and D. H. Levy,
J. Chem. Phys. 47, 1756 (1967).

21. A. Carrington, P. N. Dyer, and D. H. Levy,
J. Chem. Phys. 52, 309 (1970).

22. A. Carrington, G. N. Currie and T. A. Miller,
J. Chem. Phys. 50, 2726 (1969).

23. A. Carrington, B. J. Howard, D. H. Levy and J. C. Robertson,
Mol. Phys. 15, 187 (1968).

24. A. Carrington and B. J. Howard, Mol. Phys. 18, 225 (1970).

25. A. Carrington, A. R. Fabris and N. J. D. Lucas,
J. Chem. Phys. 49, 5545 (1969).

26. A. Carrington, A. R. Fabris and N. J. D. Lucas,
Mol. Phys. 16, 195 (1969).

27. A. Carrington, A. R. Fabris, B. J. Howard, and N. J. D. Lucas,
"Proceedings of the International Symposium on Electron and Nuclear Magnetic Resonance" (Melbourne, Australia, 1969).

28. G. C. Dousmanis, J. M. Sanders and C. H. Townes,
Phys. Rev. 100, 1735 (1955).

29. F. X. Powell and D. R. Lide, J. Chem. Phys. 41, 1413 (1964).
M. Winnewisser, K. V. L. N. Sastry, R. L. Cook and W. Gordy,
J. Chem. Phys. 41, 1687 (1964).

30. T. Amano, E. Hirota and Y. Morino, J. Mol. Spec. 27, 257 (1968).
T. Amano, S. Saito, E. Hirota, Y. Morino, D. R. Johnson and
F. X. Powell, J. Mol. Spec. 30, 275 (1969).

31. F. X. Powell and D. R. Johnson, J. Chem. Phys. 50, 4596 (1969).

32. T. Amano, S. Saito, E. Hirota and Y. Morino, J. Mol. Spec. 32, 97 (1969).

33. A. Carrington and N. J. D. Lucas, Proc. Roy. Soc. A314, 567 (1970).

34. A. A. Westenberg and N. de Haas, J. Chem. Phys. 46, 490 (1967); ibid. 47, 1393 (1967); ibid. 47, 4241 (1967); ibid. 48, 4405 (1968).

# Chapter 2

# EXPERIMENTAL

## 2.1 Introduction

The gas-phase free radicals described in this thesis are prepared by reacting the active species formed by passing a primary gas through a microwave discharge with a secondary gas inside the resonant microwave cavity. The cavity is positioned in a static magnetic field and the paramagnetic species are detected by standard e.p.r. techniques (except that electric field modulation is normally used). The radicals are usually very short lived, being quickly decomposed by collisions with other molecules present. It is thus necessary to use as low a pressure of reacting gases as possible, with the restriction that a high enough concentration of radicals is required in the microwave cavity to permit detection. Together with the problem of line-widths, a pressure in the region of 1 torr has been found optimum.

## 2.2 Spectrometer System.

Two spectrometers have been used in the study of the radicals described in this thesis. The NS spectrum was observed using a Varian V-4502 spectrometer in conjunction with a Varian 12 inch magnet (with a maximum field of 14 kilogauss) and a V-fr2503

"Fieldial" magnetic field regulator. Microwave power was supplied by an X-band klystron which operates in the region of 9 GHz and could be tuned to the frequency of the cavity. Simple A.F.C. locking to the cavity resonant frequency is used.

The CF radical was detected using a Decca X-3 spectrometer which has better inherent sensitivity. The spectrometer works at an essentially fixed frequency of 9270 MHz; the resonant frequency of the cavity has to be tuned to this. Small frequency drifts (about 1 MHz) are accommodated by a Cavity Lock system. The magnetic field was produced with a Varian 15 inch magnet with a Mark II "Fieldial"; it gives a maximum field of 15.5 kilogauss with a 4 inch magnet gap and around 22 kilogauss with a $2\frac{1}{2}$ inch gap.

Both spectrometers incorporate 100 kHz modulation together with phase sensitive detection. The output of the Varian modulation unit has been modified to give high impedance sinusoidal voltage (Stark) modulation. Facilities are also available to apply a D.C. voltage on top of the A.C. modulation; this is essential in order to observe a signal with Stark modulation. The Decca instrument however has sine- and square-wave modulation capability. The latter has a constant amplitude of modulation of approximately 300 volts peak-to-peak. It has the great advantage of giving a greater signal to noise ratio because one can modulate through the complete height of the absorption signal without fear of broadening the line. If a

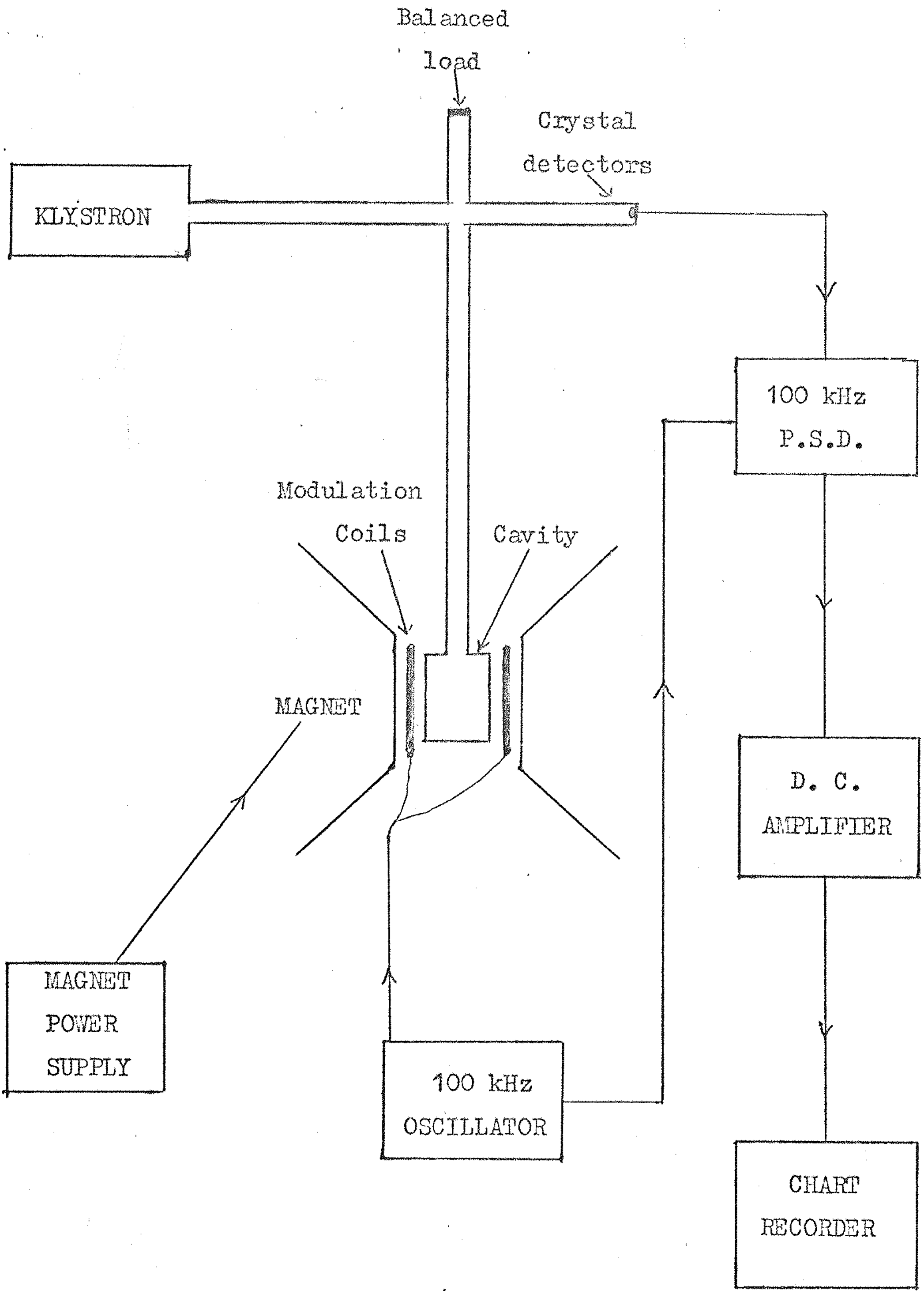


Figure 2.1 Block Diagram of Basic Spectrometer System

D.C. voltage of 150 volts is applied, the modulation is from zero to 300 volts and the spectrum consists of the straight absorption line plus a Stark shifted line of opposite phase which are usually overlapped and give the appearance of a first derivative.

A block diagram of the basic spectrometer system is given in Figure 2.1. Microwave power from the klystron is supplied to the high "Q" resonant cavity and the reflected power is detected by the crystal detectors. A slowly changing magnetic field is applied to the sample in the cavity using a "Fieldial" which controls the current passing through the magnet coils. 100 kHz modulation (electric or magnetic field) is applied across the cavity and at an absorption line, the reflected power to the crystals is also modulated at 100 kHz. The crystal current is amplified in a pre-amplifier and then demodulated by passing through a phase sensitive detector and time-constant. The resulting signal is further amplified and then displayed on chart paper or on an oscilloscope.

## 2.3 Microwave Cavity

The cavity used in the detection of NS and CF is cylindrical and operates in the $TE_{011}$ mode. In this the microwave standing wave has the electric and magnetic field pattern shown in Figure 2.2.

If the cavity is placed with its axis parallel to the

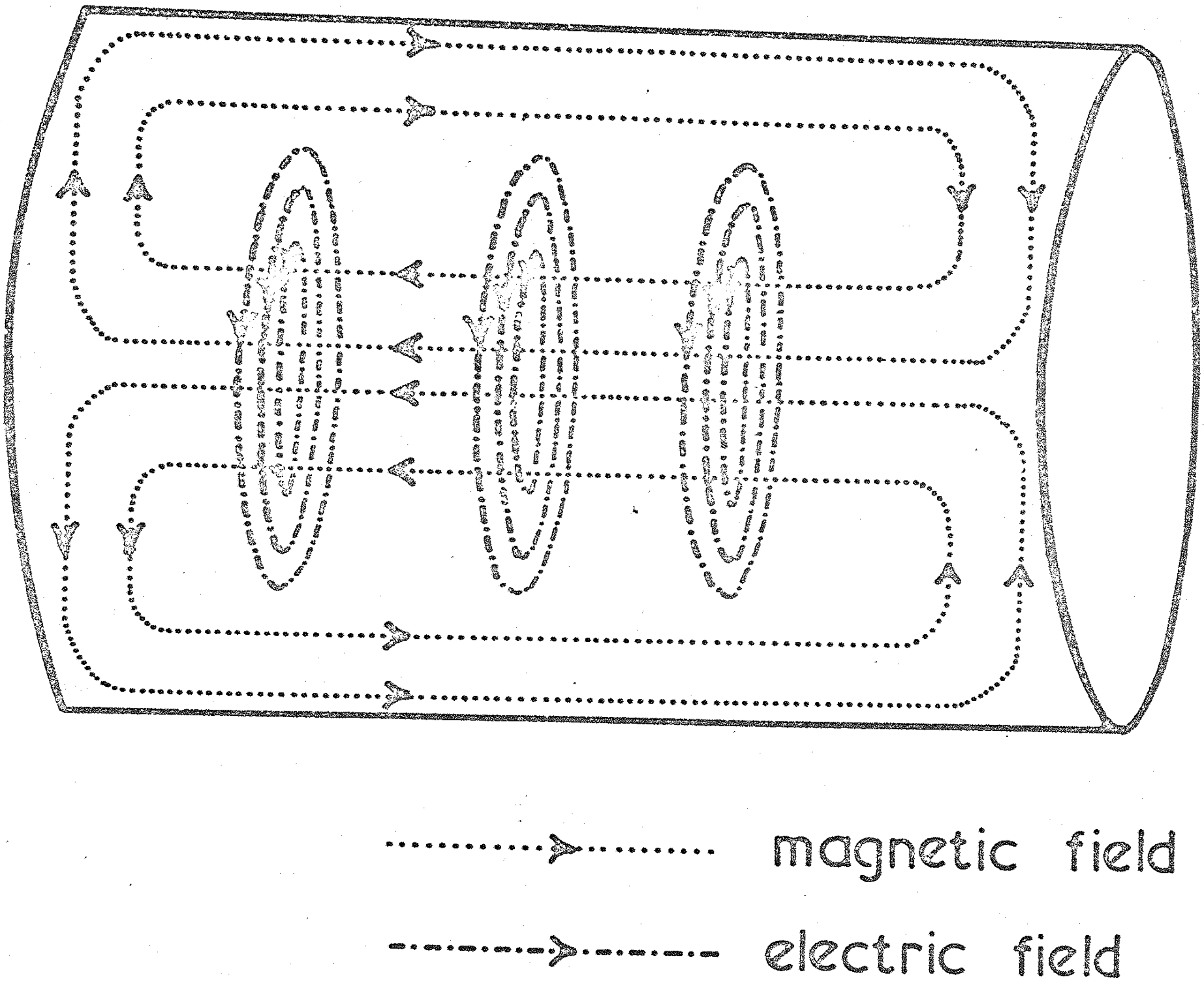


Figure 2.2 Distribution of the microwave electric and magnetic fields in

static magnetic field, the microwave electric field is everywhere perpendicular to the applied magnetic field and gives a maximum filling factor for electric dipole transitions. (N.B. the electric vector is a maximum about half-way between the centre and the cylindrical walls).

The great advantage of this mode is that no currents flow between the flat end-walls and the side-walls. This allows us to create a gap here without lowering the "Q" of the cavity significantly; in fact it actually helps to suppress modes other than those of the form $TE_{01p}$. We can then insulate the end-plates from the main cavity body and apply the Stark modulation and D.C. electric field across the end-plates.

The cavity for use on the Varian spectrometer was designed and built by Carrington, Levy and Miller [1]. It is designed to form an integral part of the vacuum system; this does away with the quartz inserts of earlier cavities and their deterioratory effect on the "Q". The cavity body and end-plates are machined from brass and gold-plated to help prevent chemical attack. The cylinder walls have two inlet ports to allow mixing of the reacting gases inside the cavity and an outlet hole on the far side; this cavity is illustrated in Figure 2.3.

The Decca cavity, built by Mr. Butcher and Mr. Cook of Decca Radar, is similar but contains a Teflon tuning stub to alter the frequency over a small range and permit exact tuning to 9270 MHz. It possesses a set of end-plates made from ceramic and covered with a thin layer of gold; this permits Zeeman modulation by means of coils affixed to the outside.

## 2.4 Vacuum System

The vacuum system is fairly simple. It consists of two gas manifolds mounted on a trolley. Each is connected to one of the entry ports or the cavity via pyrex glass tubing, employing ball and socket joints to make it flexible. At the rear of the cavity, an Edwards double-stage rotary pump, protected by a liquid nitrogen trap, maintains the flow of gas.

The primary gas ($N_2$ or $CF_4$) is admitted to one manifold from a gas storage cylinder through an Edwards needle valve, to regulate the flow. About 30 cm. upstream of the cavity, the gas passes through a microwave discharge cavity (Electro-Medical Supplies Ltd.) operating at 2450 MHz. and at a power of around 100 watts. The gas is dissociated into active species (nitrogen atoms or fluorine atoms+$CF_2$). The tubing between the discharge cavity and the microwave cavity is lined with P.T.F.E. tubing to prevent wall recombinations of atoms. It was also found desirable to have a bend in the tube between the two cavities to prevent direct photoionisation of the gas in the microwave cavity; the free electrons so formed would affect the effective magnetic and electric fields seen by the radicals and consequently render inaccurate measured field positions and dipole moments. This was found to be particularly true in the case of NS.

The secondary gas is stored in a trap at a temperature at which its vapour pressure is about 100 mm. of Hg. It is admitted to the second manifold via a needle-valve and reacts with the primary gas discharge products inside the Stark cavity.

The flows of the two gases are modified to optimise the spectrum; the total pressure as measured by an Edwards' Pirani gauge, was usually near one torr.

## 2.5 Measurement of Spectrum

Throughout the operation of the spectrometer, the klystron frequency was monitored frequently. For the Varian instrument, the microwave frequency (in the region of 9 GHZ.) was measured direct using a Hewlett-Packard H.P.5245L frequency counter with an H.P.5255A frequency converter. For the Decca spectrometer, the beat frquency (about 30 MHz.) between the microwave frequency and a known harmonic of a crystal oscillator was measured using the H.P.5245L.

The magnetic field measurements were made using n.m.r. probes in the magnet gap adjacent to the cavity. For NS, a Varian

F-8 fluxmeter with deuterium probes was used, but with considerable difficulty. The CF was measured using an AEG fluxmeter with proton probes. The spectrum was first displayed on chart paper using a Hewlett-Packard 7001A X-Y chart recorder. Then the magnetic field scan was callibrated by placing vertical pen marks when the proton or deuteron came into resonance. The resonance frequencies of the probes were measured with the H.P.5245L frequency counter.

Since the probe cannot be placed inside the cavity, a small correction to the measured magnetic field has to be made to allow for the small inhomogeneity of the field across the magnet gap and the possible distortion of the field by magnetic impurities in the cavity body. These were estimated by measuring the NO spectrum and comparing it with the calculated spectrum at the particular microwave frequency, using the experimental parameters of Brown and Radford [2].

## 2.6 Chemicals

Nitrogen ("oxygen-free") and tetrafluoromethane were supplied by the British Oxygen Co. Ltd. and Matheson Co. Ltd. They were used direct from cylinders with no further purification.

$S_2Cl_2$ and $SCl_2$ were B.D.H. Laboratory grade reagents; they were used after out-gassing by freezing down to the solid and pumping hard.

Ketene was prepared by passing acetic anhydride through a furnace at 600°C under its own vapour pressure at 30°C . The products were collected in a liquid nitrogen trap, but with continual pumping to remove volatile products like hydrogen and methane that are formed. The ketene is then purified by repeated vacuum distillation from an acetone/dry-ice trap to a liquid nitrogen trap. It was stored at liquid nitrogen temperatures to help prevent polymerisation.

# References to Chapter 2

1. A. Carrington, D. H. Levy and T. A. Miller,
Rev. Sci. Instr. 38, 1183 (1967).

T. A. Miller, Ph.D. Thesis (Cambridge, 1968).

2. R. L. Brown and H. E. Radford, Phys. Rev. 147, 147 (1966).

To see a World in a grain of sand,

And a Heaven in a wild flower,

Hold Infinity in the palm of your hand,

And Eternity in an hour.

William Blake:

Auguries of Innocence.

# Chapter 3

# THE COMPLETE MOLECULAR HAMILTONIAN

## 3.1 Introduction

The increased interest in the radio-frequency and microwave spectra of open-shell molecules (for example, the e.p.r. spectra described in this thesis) makes it necessary to obtain as complete a molecular Hamiltonian as possible in order to properly interpret the spectra and to correlate experimentally determined parameters with those calculated from electronic wavefunctions. It has been pointed out by Gerratt [1] that the most complete derivation to date is that of Curl [2], who limits himself to only those terms which are important in relating the spin-rotation and electronic g-tensors of paramagnetic molecules. As far as the author is aware, all "complete" Hamiltonians have been obtained by adding together the various interaction terms, which have been obtained separately, and assuming that the resultant is correct. In the following sections the Hamiltonian is derived as rigorously as possible within the limitations of relativistic quantum mechanics. The method of approach is outlined below.

Initially we obtain a molecular Hamiltonian expressed in space-fixed coordinates by taking the Breit equation (the two-particle form of the Dirac equation) and reducing it to non-relativistic form by a Foldy-Wouthuysen type transformation. Certain important radiative corrections, which could be obtained from quantum field theory ( e.g. that to the electron g-factor ), are introduced phenomenologically. The classical Hamiltonian, expressed in molecular coordinates, is obtained via the classical Langrangian. This is then transformed to the quantum mechanical Hamiltonian by means of a Podolsky-type transformation.

To begin with we obtain the Hamiltonian appropriate to a general non-linear molecule. This is then followed by a parallel developement for the linear molecule with all its incipient difficulties (because it has only two rotational degrees of freedom). Throughout this work all external electromagnetic fields are assumed to be constant.

## 3.2 Space-fixed Hamiltonian

The energy of a single electron in an external electromagnetic field is well described by the Dirac equation [3,4,5] which is the simplest first order operator that is Lorentz invariant (i.e. is unchanged in form by any orthogonal space-time transformation) and satisfies the Klein-Gordon equation. Such a Hamiltonian is;

$$\mathcal{H}_D = c\underline{\alpha}.\underline{\pi} + \phi + \beta mc^2 \qquad (3.1)$$

where $\underline{\pi} = \underline{p} + \frac{e}{c}\underline{A}$ is the mechanical momentum, $\underline{p}$ is the conjugate (canonical) momentum, $\phi$ is the scalar potential and $\underline{A}$ is the vector potential of the electromagnetic field ( $\underline{\nabla}_\wedge \underline{A} = \underline{H}$, the static magnetic field). In the simplest representation $\underline{\alpha}$ and $\beta$ are 4x4 matrices related to the Pauli spin matrices $\underline{\sigma}$ :

$$\underline{\alpha} = \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} ; \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{3.2}$$

and in the representation with $\sigma_z$ diazonal :

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} ; \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \tag{3.3}$$

I is the 2-dimensional unit matrix. The wavefunction is a 4-dimensional spinor. To first order, two solutions have energy $mc^2$ and the other two $-mc^2$. These are mixed by $\alpha$ (a so-called odd operator). In any physical problem, it is desirable to reduce the Dirac equation to a "non-relativistic form" by a Foldy-Wouthuysen[6] unitary transformation, where the odd terms are made negligible. This gives the energy in a descending power series in c (the velocity of light), with leading term $mc^2$.

In the case of two electrons, it is not possible to write an exact relativistic equation; however the Breit equation [7] for two electrons is correct (i.e. Lorentz invariant) to order $c^{-2}$.

$$= c\underline{\alpha}_1\cdot\underline{\Pi}_1 + c\underline{\alpha}_2\cdot\underline{\Pi}_2 + e_1\phi + e_2\phi + m_1c^2 + m_2c^2$$

$$+ \frac{e_1e_2}{r}\left[1 - \frac{\underline{\alpha}_1\cdot\underline{\alpha}_2}{2} - \frac{(\underline{\alpha}_1\cdot\underline{r})(\underline{\alpha}_2\cdot r)}{2r^2}\right] \qquad (3.4)$$

This has been reduced to a non-relativistic form by Chraplyvy [8] and Barker and Glover [9]. The resulting Hamiltonian correct to order $c^{-2}$ is :

$$\mathcal{H} = \sum_i \Bigg[ m_ic^2 + \frac{1}{2m_i}\Pi_i^2 - e_i\phi_i + \sum_{j\neq i}\frac{e_ie_j}{2R} \qquad (3.5a)$$

$$+ \frac{g_i\hbar e_i}{2m_ic}(\underline{s}_i\cdot\underline{H}_i) \qquad (3.5b)$$

$$- \frac{g_i\hbar e_i}{8m_i^2c^2}\,\underline{s}_i\cdot(\underline{\Pi}_i\wedge\underline{E}_i - \underline{E}_i\wedge\underline{\Pi}_i) \qquad (3.5c)$$

$$+ \frac{\hbar^2e_i}{8m_i^2c^2}(\underline{\nabla}\cdot\underline{E}_i) \qquad (3.5d)$$

$$- \frac{1}{8m_i^3c^2}\Pi_i^4 - \frac{g_i\hbar e_i}{4m_i^3c^3}(\underline{s}_i\cdot\underline{H})\,\Pi_i^2 \qquad (3.5e)$$

$$+\sum_{j\neq i}\Big\{-\frac{e_i e_j}{4m_i m_j c^2}\,\underline{\Pi}_i\cdot\Big(\frac{1}{R}+\underline{R}\,\frac{1}{R^3}\,\underline{R}\Big)\cdot\underline{\Pi}_j \qquad (3.5f)$$

$$-\frac{g_i e_i e_j \hbar}{4m_i^2 c^2 R^3}\,\underline{s}_i\cdot(\underline{R}\wedge\underline{\Pi}_i) \qquad (3.5g)$$

$$+\frac{g_i e_i e_j \hbar}{2m_i m_j c^2 R^3}\,\underline{s}_i\cdot(\underline{R}\wedge\underline{\Pi}_j) \qquad (3.5h)$$

$$-\frac{e_i e_j \hbar^2 \pi}{2m_i^2 c^2}\,\delta(R) \qquad (3.5i)$$

$$+\frac{g_i g_j e_i e_j \hbar^2}{8m_i m_j c^2}\Big(\frac{1}{R^3}\,(\underline{s}_i\cdot\underline{s}_j)-\frac{3}{R^5}\,(\underline{s}_i\cdot\underline{R})(\underline{s}_j\cdot\underline{R})$$

$$-\frac{8\pi}{3}\,\delta(R)(\underline{s}_i\cdot\underline{s}_j)\Big)\Big\}\Big] \qquad (3.5j)$$

$$+\,O(c^{-3})\ ,$$

where i and j are electron subscripts (in the case of two electrons 1 or 2), $m_i$, $-e_i$, $\underline{s}_i$, $g_i$, $\underline{R}_i$ and $\underline{\Pi}_i$ are the mass, charge, spin angular momentum, g-factor, position vector and mechanical momentum of electron i. Also :

$$\underline{R} = \underline{R}_{ij} = \underline{R}_i - \underline{R}_j\ ,$$

and $\delta(R)$ is the Dirac delta function. Throughout this work the fields are assumed to be homogeneous and constant in time; therefore the subscripts to $\underline{A}$ and $\phi$ may be dropped.

The significance of the various terms in equation (3.5) is as follows : (5a) represents the classical interaction terms for electrons in an electromagnetic field, namely their rest mass, kinetic energy, interaction with an external electric potential and the Coulomb interaction between two electrons. (5b) gives the interaction of the spin magnetic moment with the external magnetic field. Relativistically a moving spin magnetic moment has an electric moment perpendicular to it and its velocity and the interaction of this with the external electric field is represented by (5c); alternatively, to a moving charge, the electric field appears to have some magnetic character which can then interact with the electron spin. This term has been considered by Thomas [11]. For homogeneous electric fields (5c) simplifies to :

$$+ \frac{g_i h e_i}{4 m_i^2 c^2} \underline{s}_i \cdot (\underline{E} \wedge \underline{\Pi}_i) \qquad (3.5c')$$

For the same reason (5d) vanishes; this is the Darwin term which represents the interaction due to the spreading out of the charge of the electron or so-called Zitterbewegung (see for example ref. 4). (5e) gives the relativistic corrections to the electron kinetic energy and the Zeeman interaction. The latter term has been included even though formally of order $c^{-3}$ because it arises in the reduction of the Dirac equation for one electron in the same way that corrections to the orbital Zeeman are obtained from the former term, and also it has been shown to be important spectroscopically [11,12]. The retarded interaction (5f) of the charge of one electron with the electromagnetic field due to the other electron (orbit-orbit interaction) has been derived classically by Darwin [13]. The spin-orbit and spin-other-orbit interactions are given by (5g) and (5h). (5i) is similar to the Darwin term (5d) but is a correction due to the electric field of the other electrons. It can be interpreted as a spread of the electron charge and to a first approximation is the modification to the Coulomb interaction (5a) provided by a spherically charge distribution of mean square radius $\langle r^2 \rangle = \frac{3}{4}(h/mc)^2$. The final term (5j) is the spin-spin interaction. The former represents the classical dipole-dipole interaction and the latter expresses the mutual interaction between two mutually penetrating magnetic moments (the Fermi-contact term). Asimilar Hamiltonian has been obtained by Itoh [14] using quantum electrodynamics.

We now wish to extend this Hamiltonian to a molecule but before this can be done a number of modifications and assumptions have to be made. First, it is assumed that there are no three particle interactions; this has been confirmed to order $c^{-2}$ by Itoh [14] for a system of many electrons. Secondly, the value of the electron g-factor in equation (3.5) is exactly 2, whereas the experimental value is 2.002319; this discrepancy can be accounted for if we use quantum electrodymamics. In this work the experimental value will be used; other radiative corrections will be neglected even though the Lamb shift [15] may be important in the observation of electronic transitions. Thirdly, the Hamiltonian must be extended to include nuclei, which are not Dirac particles and have anomalous magnetic moments. These particles are included by assuming that they behave like Dirac particles, but having the magnetic moments given by experiment. Bethe and Salpeter [15] (page 194) have shown that this assumption is allowed provided that terms involving only (nuclear mass)$^{-1}$ are retained. The terms of higher order in nuclear mass are all formally of order $c^{-2}$ and are negligible. Finally, the possibility of nuclear quadrupole interactions may be included phenomenologically by adding $\mathcal{H}_Q$; its form will not concern us here, but is given by many authors.

From now on we shall use the subscripts $\alpha$ and $\beta$ to distinguish the nuclei. $Z_\alpha$ will be the atomic number of nucleus $\alpha$, $\beta = \frac{eh}{2mc}$ the Bohr magneton and $\beta_N = \frac{eh}{2m_p c}$ the nuclear magneton; $m_p$ is the proton mass. Dropping the subscripts from electron mass, charge and g-factor the complete molecular Hamiltonian in the space-fixed coordinate system is :

$$
\begin{aligned}
\mathcal{H} = \sum_i \Bigg\{ & \frac{1}{2m}\pi_i^2 - \frac{1}{8m^3c^2}\pi_i^4 + \frac{g\beta}{2mc}\,\underline{s}_i\cdot(\underline{E}\wedge\underline{\Pi}_i) - \frac{g\beta}{2m^2c^2}(\underline{s}_i\cdot\underline{H})\,\pi_i^2 \\
& + \sum_{j\neq i}\Bigg[ - \frac{e^2}{4m^2c^2}\,\underline{\Pi}_i\cdot\Big(\frac{1}{R_{ij}} + \underline{R}_{ij}\frac{1}{R_{ij}^3}\underline{R}_{ij}\Big)\cdot\underline{\Pi}_j \\
& \qquad + \frac{g\beta e}{2mc}\frac{1}{R_{ij}^3}\,\underline{s}_i\cdot\underline{R}_{ij}\wedge(2\,\underline{\Pi}_j - \underline{\Pi}_i)\Bigg] \\
& + \sum_\alpha \Bigg[ \frac{Z_\alpha e^2}{2mm_\alpha c^2}\,\underline{\Pi}_i\cdot\Big(\frac{1}{R_{i\alpha}} + \underline{R}_{i\alpha}\frac{1}{R_{i\alpha}^3}\underline{R}_{i\alpha}\Big)\cdot\underline{\Pi}_\alpha \\
& \qquad - \frac{Z_\alpha g_N e}{2c}\frac{1}{R_{i\alpha}^3}\,\underline{s}_i\cdot\underline{R}_{i\alpha}\wedge\Big(\frac{2}{m_\alpha}\underline{\Pi}_\alpha - \frac{1}{m}\underline{\Pi}_i\Big) \\
& \qquad + \frac{g_\alpha\beta_N e}{mc}\frac{1}{R_{i\alpha}^3}\,\underline{I}_\alpha\cdot\underline{R}_{i\alpha}\wedge\underline{\Pi}_i\Bigg]\Bigg\} \\
& + \sum_\alpha \frac{1}{2m_\alpha}\Pi_\alpha^2 + V + O(c^{-3}). \qquad (3.6)
\end{aligned}
$$

In this Hamiltonian :

$$\underline{\Pi}_\alpha = \underline{P}_\alpha - \frac{Z_\alpha e}{c}\underline{A}_\alpha \qquad (3.7)$$

and V which contains all terms not involving $\underline{\Pi}_i$ or $\underline{\Pi}_\alpha$ is given by :

$$V = \sum_i \Bigg\{ mc^2 - e\phi_i + g\beta\,\underline{s}_i\cdot\underline{H} + \sum_{j\neq i}\Bigg\{ \frac{e^2}{2R_{ij}} - \frac{e^2\hbar^2}{2m^2c^2}\,\delta(R_{ij})$$

$$+ \tfrac{1}{2} g^2\beta^2\left[\frac{1}{R_{ij}^3}\,\underline{s}_i\cdot\underline{s}_j - \frac{3}{R_{ij}^5}\,(\underline{s}_i\cdot\underline{R}_{ij})(\underline{s}_j\cdot\underline{R}_{ij}) - \frac{8\pi}{3}\,\delta(R_{ij})\,\underline{s}_i\cdot\underline{s}_j\right]\Bigg\}$$

$$+\sum_{\alpha}\Bigg\{-\frac{Z_\alpha e^2}{R_{i\alpha}} + \frac{Z_\alpha e^2\hbar^2}{2m^2c^2}\,\delta(R_{i\alpha})$$

$$- g g_\alpha \beta\beta_n\left[\frac{1}{R_{i\alpha}^3}\,\underline{s}_i\cdot\underline{I}_\alpha - \frac{3}{R_{i\alpha}^5}(\underline{s}_i\cdot\underline{R}_{i\alpha})(\underline{I}_\alpha\cdot\underline{R}_{i\alpha}) - \frac{8\pi}{3}\,\delta(R_{i\alpha})\,\underline{s}_i\cdot\underline{I}_\alpha\right]\Bigg\}\Bigg\}$$

$$+\sum_{\alpha}\Bigg\{m_\alpha c^2 + Z_\alpha e\phi_\alpha - g_\alpha\beta_N\underline{I}_\alpha\cdot\underline{H} + \sum_{\beta\neq\alpha}\frac{Z_\alpha Z_\beta e^2}{2R_{\alpha\beta}}\Bigg\} + \mathcal{H}_Q \qquad (3.8)$$

The transformation of V to molecular coordinates is trivial. Since $\underline{\Pi}_i$ and $\underline{\Pi}_\alpha$ both contain magnetic vector potential terms of order $c^{-1}$, the Hamiltonian (3.6) contains terms of high order in c which are formally negligible, but we retain them to maintain the gauge invariance of the Hamiltonian (see for example ref. 4) ; in any application these terms may be dropped after the choice of a suitable gauge. In the derivation of this Hamiltonian the anomalous magnetic moments of the electrons and nuclei have been introduced after a Foldy-Wouthuysen type transformation. Hegstrom [16], who considered the hydrogen atom, introduced these effects before the Foldy-Wouthuysen type reduction and has obtained slightly different results for the spin-orbit coupling terms. If the g-factor of an electron is written as g = 2(1 + a) his spin-orbit coupling terms are proportional to (1 + 2a) in contrast to ours which is proportional to (1 + a). An appeal to quantum electrodynamics is necessary to decide which is correct, but the author is not aware of such a study.

Since the difficulties that arise in transforming the Hamiltonian to a molecular coordinate system involve only the momenta, we may write equation (3.6) in the simpler form :

$$\mathcal{H} = \sum_i \frac{1}{2m}\pi_i^2 + \underline{B}_i\cdot\underline{\pi}_i + C\,\pi_i^4 + \sum_j \underline{\pi}_i\cdot\underline{\underline{D}}_{ij}\cdot\underline{\pi}_j + \sum_\alpha \underline{\pi}_i\cdot\underline{\underline{D}}_{i\alpha}\cdot\underline{\pi}_\alpha$$

$$+ \sum_\alpha \left\{ \frac{1}{2m_\alpha}\pi_\alpha^2 + \underline{B}_\alpha\cdot\underline{\pi}_\alpha \right\} + V + O(c^{-3}). \qquad (3.9)$$

The expressions $\underline{B}$, C and $\underline{\underline{D}}$ (a tensor) are all of order $c^{-2}$ and are given by :

$$\underline{B}_i = \frac{g\beta}{2mc}(\underline{s}_i \wedge \underline{E}) - \sum_{j\neq i} \frac{g\beta e}{2mc}\frac{1}{R_{ij}^3}\left[2(\underline{s}_j \wedge \underline{R}_{ij}) + (\underline{s}_i \wedge \underline{R}_{ij})\right]$$

$$+ \sum_\alpha \frac{Z_\alpha g\beta e}{2mc}\frac{1}{R_{i\alpha}^3}(\underline{s}_i \wedge \underline{R}_{i\alpha}) + \frac{g_\alpha \beta_N e}{mc}\frac{1}{R_{i\alpha}^3}(\underline{I}_\alpha \wedge \underline{R}_{i\alpha}) , \qquad (3.10)$$

$$\underline{B}_\alpha = -\sum_i \frac{Z_\alpha g\beta e}{m_\alpha c}\frac{1}{R_{i\alpha}^3}(\underline{s}_i \wedge \underline{R}_{i\alpha}) , \qquad (3.11)$$

$$C = -\frac{1}{8m^3c^2} , \qquad (3.12)$$

$$\underline{\underline{D}}_{ij} = - \delta_{ij} \frac{g\beta}{2m^2c^2} \underline{s}_i \cdot \underline{H} - (1 - \delta_{ij}) \frac{e^2}{4m^2c^2} \left(\frac{1}{R_{ij}} + \underline{R}_{ij} \frac{1}{R_{ij}^3} \underline{R}_{ij}\right) , \tag{3.13}$$

and

$$\underline{\underline{D}}_{i\alpha} = \frac{Z_\alpha e^2}{2mm_\alpha c^2} \left(\frac{1}{R_{i\alpha}} + \underline{R}_{i\alpha} \frac{1}{R_{i\alpha}^3} \underline{R}_{i\alpha}\right) . \tag{3.14}$$

Equation (3.5) is the quantum mechanical Hamiltonian, but the classical Hamiltonian is given by the same expression.

### 3.3 Transformation of Classical Hamiltonian from Space-fixed to Molecule-fixed Axes.

The classical Hamiltonian (3.6) is difficult to transform directly because it is expressed in terms of momenta. We shall follow a method similar to that of Curl $^2$ and use a classical Langrangian as an intermediary; the advantage of the Lagrangian is that it is a function of velocities, which are easier to transform. Classically the Lagrangian, $\mathcal{L}$, and the velocities, $\dot{\underline{R}}_k$, of a system of particles are related to the Hamiltonian, $\mathcal{H}$, and the conjugate momenta, $P_k$, by :

$$P_k = \frac{\partial \mathcal{L}}{\partial R_k} , \tag{3.15}$$

and

$$\mathcal{H} = \sum_k P_k \dot{R}_k - \mathcal{L} . \tag{3.16}$$

For the Lagrangian :

$$\mathcal{L} = \sum_i \left\{ \tfrac{1}{2} m \dot{\underline{R}}_i^2 - \frac{e}{c} \underline{A}_i \cdot \dot{\underline{R}}_i - m \underline{B}_i \cdot \dot{\underline{R}}_i - m^4 C \dot{R}_i^4 - \sum_j m^2 \dot{\underline{R}}_i \cdot \underline{\underline{D}}_{ij} \cdot \dot{\underline{R}}_j \right.$$

$$\left. - \sum_\alpha m m_\alpha \dot{\underline{R}}_i \cdot \underline{\underline{D}}_{i\alpha} \cdot \dot{\underline{R}}_\alpha \right\} + \sum_\alpha \left\{ \tfrac{1}{2} m_\alpha \dot{R}_\alpha^2 + \frac{Z_\alpha e}{c} \underline{A}_\alpha \cdot \dot{\underline{R}}_\alpha \right.$$

$$\left. - m_\alpha \underline{B}_\alpha \cdot \dot{\underline{R}}_\alpha \right\} - V + O(c^{-3}) , \qquad (3.17)$$

we obtain the conjugate momenta ;

$$\underline{P}_i = m \dot{\underline{R}}_i - \frac{e}{c} \underline{A}_i - m \underline{B}_i - 4 m^4 C \dot{R}_i^2 \dot{\underline{R}}_i - \sum_j 2 m^2 \underline{\underline{D}}_{ij} \cdot \dot{\underline{R}}_j$$

$$- \sum_\alpha m m_\alpha \underline{\underline{D}}_{i\alpha} \cdot \dot{\underline{R}}_\alpha + O(c^{-3}) \qquad (3.18)$$

and

$$\underline{P}_\alpha = m_\alpha \dot{\underline{R}}_\alpha + \frac{Z_\alpha e}{c} \underline{A}_\alpha - m_\alpha \underline{B}_\alpha - \sum_i m m_\alpha \underline{\underline{D}}_{i\alpha} \cdot \dot{\underline{R}}_i + O(c^{-3}) . \qquad (3.19)$$

Substitution into equations (3.17) and (3.16) gives the same Hamiltonian as (3.19) and we are thus justified in using (3.17) as our Lagrangian.

The Lagrangian includes relativistic corrections and it might be thought that we should use a Lorentz transformation when transforming to molecular coordinates. This would be true if we were performing our physical measurements while moving with the molecule. Instead we measure quantities like energy differences and electric or magnetic fields in a laboratory fixed frame. The Lagrangian should be appropriate to the laboratory frame, whether space or molecular coordinates are used, and a classical or Galilean transformation should be used; that is to say we only perform a transformation of variables within the space-fixed frame of reference.

In performing the transformation, it is necessary to separate translational, rotational, vibrational and electronic motion as completely as possible. This is done in three stages :

(a) change the origin of coordinates from a space-fixed one to the molecular centre of mass, $\underline{R}$, keeping the axes parallel to the original space-fixed axes; this separates off the translational motion.

(b) without changing the origin, allow the axes to rotate with the molecule with velocity $\underline{\omega}$ ; this separates off rotation.

(c) move the origin to the centre of mass of the nuclei without changing the orientation of the axes.

This is analogous to the method of Wilson and Howard [17], or as detailed in chapter 11 of Wilson, Decius and Cross [18].

If the subscript $\lambda$ is used to denote $\alpha$ or i, the old coordinates, $\underline{R}_\lambda$, can be written in terms of the new coordinates $\underline{r}_\lambda$ as :

$$\underline{R}_\lambda = \underline{R} + \underline{r}_\lambda + \underline{\delta} \qquad (3.20)$$

where $\underline{R}$ is the position of the centre of mass of the molecule :

$$\underline{R} = \frac{1}{M}\sum_{\lambda} m_{\lambda}\underline{R}_{\lambda} = \frac{1}{M}\left[\sum_{\alpha} m_{\alpha}\underline{R}_{\alpha} + \sum_{i} m\underline{R}_{i}\right] \tag{3.21}$$

where M is the total mass of the molecule ( $= \sum_{\lambda} m_{\lambda}$ ), and where $\underline{\delta}$ is the position of the centre of mass of the nuclei relative to the centre of mass of the complete molecule.

$$\underline{\delta} = -\frac{m}{M}\sum_{i} \underline{r}_{i} \tag{3.22}$$

It should also be noted that because of condition (c) :

$$m_{\alpha}\underline{r}_{\alpha} = 0 \tag{3.23}$$

Since $\underline{\omega}$ is the angular velocity of the molecular axes with respect to the space-fixed axes, the time derivative of (3.21) is :

$$\dot{\underline{R}}_{\lambda} = \dot{\underline{R}} + \dot{\underline{r}}_{\lambda} + \dot{\underline{\delta}} + (\underline{\omega}\wedge\underline{r}_{\lambda}) + (\underline{\omega}\wedge\underline{\delta}) \tag{3.24}$$

where the components of $\underline{r}_{\lambda}$ (and $\underline{\delta}$ ) are measured in the moving axis system.

Before we consider the transformation of the Lagrangian (3.17) to molecule-fixed axes, we perform the transformation in the absence of external fields and magnetic effects between particles. Then the space-fixed Lagrangian becomes :

$$\mathcal{L} = \sum_i \tfrac{1}{2} m \dot{R}_i^2 + \sum_\alpha \tfrac{1}{2} m_\alpha \dot{R}_\alpha^2 - V \qquad (3.25)$$

Rewriting $\underline{R}_\lambda$ in terms of molecular velocities, equation (3.25) becomes :

$$\begin{aligned}\mathcal{L} = {} & M\dot{\underline{R}}^2 + \sum_\alpha m_\alpha(\underline{\omega}\wedge(\underline{r}_\alpha + \underline{\delta})).(\underline{\omega}\wedge(\underline{r}_\alpha + \underline{\delta})) + \sum_\alpha m_\alpha(\dot{\underline{r}}_\alpha + \dot{\underline{\delta}})^2 \\ & + \sum_i m_i(\underline{\omega}\wedge(\underline{r}_i + \underline{\delta})).(\underline{\omega}\wedge(\underline{r}_i + \underline{\delta})) + \sum_i m_i(\dot{\underline{r}}_i + \dot{\underline{\delta}})^2 \\ & + 2\underline{\omega}.\Big[\sum_\alpha m_\alpha(\underline{r}_\alpha + \dot{\underline{\delta}})\wedge(\dot{\underline{r}}_\alpha + \dot{\underline{\delta}}) + \\ & \qquad + \sum_i m(\underline{r}_i + \underline{\delta}) \;\; (\dot{\underline{r}}_i + \dot{\underline{\delta}})\Big] - 2V \end{aligned} \qquad (3.26)$$

or expanding in terms of molecular coordinates :

$$\begin{aligned}\mathcal{L} = {} & MR^2 + I_{xx}\omega_x^2 + I_{yy}\omega_y^2 + I_{zz}\omega_z^2 + 2I_{xy}\omega_x\omega_y \\ & + 2I_{yz}\omega_y\omega_z + 2I_{zx}\omega_z\omega_x + \sum_\alpha m_\alpha \dot{r}_\alpha^2 + \sum_i m\dot{r}_i^2 - M\dot{\delta}^2 \\ & + 2\underline{\omega}.\Big[\sum_\alpha m_\alpha(\underline{r}_\alpha\wedge\dot{\underline{r}}_\alpha) + \sum_i m(\underline{r}_i\wedge\mathring{\underline{r}}_i) - M\,\underline{\delta}\wedge\dot{\underline{\delta}}\Big] - 2V \end{aligned} \qquad (3.27)$$

where :

$$I_{xx} = \sum_\alpha m_\alpha(y_\alpha^2 + z_\alpha^2) + \sum_i m(y_i^2 + z_i^2) - \frac{1}{M}\Big[(\sum_i my_i)^2 + (\sum_i mz_i)^2\Big]$$

and similarly $I_{yy}$ and $I_{zz}$ (3.28)

Also :

$$-I_{xy} = \sum_\alpha m_\alpha x_\alpha y_\alpha + \sum_i mx_i y_i - \frac{1}{M}(\sum_i mx_i)(\sum_i my_i) \qquad (3.29)$$

$I_{yz}$ and $I_{zx}$ are similarly defined.

So far the orientation of the molecule fixed axes has been left undetermined. The method used by Wilson and Howard and used here is the Eckart condition [20].

$$\sum_{\alpha} m_{\alpha} \underline{r}^{o}_{\alpha} \wedge \underline{r}_{\alpha} = 0 \tag{3.30}$$

where $\underline{r}^{o}_{\alpha}$ is the equilibrium value of $\underline{r}_{\alpha}$. This condition gives $\sum_{\alpha} \underline{r}^{o}_{\alpha} \wedge \underline{r}_{\alpha} m_{\alpha} = 0$, which is almost equivalent to there being no angular momentum of the nuclei relative to the rotating axis system.

The nuclear displacements, $\underline{r}_{\alpha} - \underline{r}^{o}_{\alpha}$, are now written in terms of the normal coordinates $Q_r$,

$$\sqrt{m}_{\alpha} (\underline{r}_{\alpha} - \underline{r}^{o}_{\alpha}) = \sum_{r} \underline{\ell}_{\alpha r} Q_r \tag{3.31}$$

The elements $\underline{\ell}_{\alpha r}$ obey a number of orthogonality relationships :

$$\sum_{\alpha} \underline{\ell}_{\alpha r} \cdot \underline{\ell}_{\alpha s} = \delta_{rs} \tag{3.32}$$

$$\sum_{\alpha} \sqrt{m}_{\alpha} \underline{\ell}_{\alpha r} = 0 \tag{3.33}$$

$$\sum_{\alpha} \sqrt{m}_{\alpha} (\underline{r}^{o} \wedge \underline{\ell}_{\alpha r}) = 0 \tag{3.34}$$

These represent respectively the orthogonality between the vibrational modes, between vibrations and translation, and between vibrations and rotation. In terms of normal coordinates, the nuclear Coriolis coupling in (3.27) can be written as :

$$\sum_{\alpha} (\underline{r}_{\alpha} - \underline{r}^{0}_{\alpha}) \wedge \dot{\underline{r}}_{\alpha} = \underline{\zeta}_{rs} Q_r \dot{Q}_s \tag{3.35}$$

(summation over r and s assumed)

where $\zeta_{rs}$ is the Coriolis coupling constant :

$$\zeta_{rs} = \sum_{\alpha} \underline{\ell}_{\alpha r} \wedge \underline{\ell}_{\alpha s} \tag{3.36}$$

Then the total Lagrangian is given by :

$$\begin{aligned} 2\mathcal{L} = {} & M\dot{R}^2 + I_{xx}\omega_x^2 + I_{yy}\omega_y^2 + I_{zz}\omega_z^2 \\ & + 2I_{xy}\omega_x\omega_y + 2I_{yz}\omega_y\omega_z + 2I_{zx}\omega_z\omega_x \\ & + 2\omega_x\Big[\zeta^{x}_{rs}Q_r\dot{Q}_s + \sum_i m(y_i\dot{z}_i - z_i\dot{y}_i) - \frac{m}{M}\sum_{i,j}(y_i\dot{z}_j - z_i\dot{y}_j)\Big] \\ & + 2\omega_y\Big[\zeta^{y}_{rs}Q_r\dot{Q}_s + \sum_i m(z_i\dot{x}_i - x_i\dot{z}_i) - \frac{m}{M}\sum_{i,j}(z_i\dot{x}_j - x_i\dot{z}_j)\Big] \\ & + 2\omega_z\Big[\zeta^{z}_{rs}Q_r\dot{Q}_s + \sum_i m(x_i\dot{y}_i - y_i\dot{x}_i) - \frac{m}{M}\sum_{i,j}(x_i\dot{y}_j - y_i\dot{x}_j)\Big] \\ & + \sum_r \dot{Q}_r^2 + \sum_i m\dot{r}_i^2 - \frac{m^2}{M}\Big(\sum_i \underline{r}_i\Big)^2 - 2V \end{aligned} \tag{3.37}$$

It is now necessary to express the Lagrangian and then the Hamiltonian in terms of momenta instead of velocities.

The components of translational momenta are given by :

$$\underline{P} = \frac{\partial \mathcal{L}}{\partial \dot{\underline{R}}} = M\dot{\underline{R}} \qquad (3.38)$$

The angular momentum conjugate to $\omega_x$ is $J_x = \frac{\partial \mathcal{L}}{\partial \omega_x}$

$$J_x = I_{xx}\omega_x - I_{xy}\omega_y - I_{xz}\omega_z + \sum_{r,s} \zeta^x_{rs} Q_r \dot{Q}_s$$

$$+ \sum_i m(y_i \dot{z}_i - z_i \dot{y}_i) - \frac{m^2}{M}\sum_{i,j}(y_i \dot{z}_j - z_i \dot{y}_j) \qquad (3.39)$$

Exactly analogous expressions are obtained for $M_y$ and $M_z$. Similarly the momentum conjugate to $Q_s$ is :

$$P_s = \frac{\partial \mathcal{L}}{\partial \dot{Q}_s} = \dot{Q}_s + \sum_r \underline{\omega}.\underline{\zeta}_{rs} Q_r \qquad (3.40)$$

and the electron momenta $\underline{p}_i$ conjugate to $\underline{r}_i$ are :

$$\underline{p}_i = m\dot{\underline{r}}_i - \frac{m^2}{M}\sum_j \dot{\underline{r}}_j + \underline{\omega}_\wedge\left(m\underline{r}_i - \frac{m^2}{M}\sum_j \underline{r}_j\right) \qquad (3.41)$$

Substituting (3.40) and (3.41) into (3.39) gives :

$$J_x = I_{xx}\omega_x - I_{xy}\omega_y - I_{xz}\omega_z + \sum_{r,s} \zeta^x_{rs} Q_r\left(P_s - \sum_t \underline{\omega}.\underline{\zeta}_{ts} Q_t\right)$$

$$+ \sum_i (\underline{r}_i \wedge \underline{p}_i)_x - \omega_x\left\{\sum_i m(y_i^2 + z_i^2) - \frac{m}{M}\left[\left(\sum_i y_i\right)^2 + \left(\sum_i z_i\right)^2\right]\right\}$$

$$+ \omega_y\left\{\sum_i m x_i y_i - \frac{m}{M}\left(\sum_i x_i\right)\left(\sum_i y_i\right)\right\}$$

$$+\ \omega_z \left\{ \sum_i m x_i z_i \ - \ \frac{m^2}{M} \left( \sum_i x_i \right) \left( \sum_i z_i \right) \right\} \tag{3.42}$$

Now $\sum_{r,s} \zeta^x_{rs} Q_r P_s$ corresponds to a component of angular momentum of the nuclei, $G_x$, and $\sum_i (\underline{r}_i \wedge \underline{p}_i)_x$ is the x-component of the total orbital angular momentum, $L_x$ :

$$J_x = I'_{xx}\omega_x + I'_{xy}\omega_y + I'_{xz}\omega_z + G_x + L_x \tag{3.43}$$

where the moments of inertia have been redefined as :

$$I'_{xx} = \sum_\alpha m_\alpha (y_\alpha^2 + z_\alpha^2) \ - \sum_{r,s,t} \zeta^x_{ts} \zeta^x_{rs} Q_t Q_s \tag{3.44}$$

$$I'_{xy} = \sum_\alpha m_\alpha (x_\alpha y_\alpha) \ + \sum_{r,s,t} \zeta^x_{ts} \zeta^y_{rs} Q_t Q_r \tag{3.45}$$

and similarly $I'_{xz}$. Analogous expressions for the other components of $\underline{J}$ are obtained, giving in matrix notation :

$$\underline{J} - \underline{L} - \underline{G} = \underline{\underline{I}}' . \underline{\omega} \tag{3.46}$$

For a non-linear molecules $\underline{\underline{I}}'$ is non-singular, so that inversion is permitted.

$$\therefore \quad \underline{\omega} = \underline{\underline{\mu}} . ( \underline{J} - \underline{L} - \underline{G} ) \tag{3.47}$$

where $\underline{\underline{\mu}}$ is the inverse matrix of $\underline{\underline{I}}'$.

However from (3.37) :

$$2\mathcal{L} = \frac{P^2}{M} + \underline{\omega}.\underline{J} + \sum_r P_r \dot{Q}_r + \sum_i \underline{p}_i . \dot{\underline{r}}_i - 2V \tag{3.48}$$

Then using equation (3.16) and replacing $(\underline{J} - \underline{L} - \underline{G})$ by $\underline{N}$, the rotational angular momentum, we obtain :

$$\mathcal{H} = \frac{P^2}{2M} + \tfrac{1}{2}\underline{N}\cdot\underline{\underline{\mu}}\cdot\underline{N} + \tfrac{1}{2}\sum_r P_r^2 + \frac{1}{2m}\sum_i p_i^2 + \frac{1}{2M_N}\Big(\sum_i \underline{p}_i\Big)^2 + V \tag{3.49}$$

where $M_N$ is the total nuclear mass.

In passing, it is useful to note that the new momenta are related to the momenta in the space-fixed coordinates by :

$$\underline{P} = \sum_i \underline{P}_i + \sum_\alpha \underline{P}_\alpha \tag{3.50}$$

$$\underline{N} = \sum_\alpha (\underline{r}_\alpha \wedge \underline{P}_\alpha) - \sum_\alpha \frac{1}{\sqrt{m_\alpha}}\, \underline{\zeta}_{rs} Q_r (\underline{\ell}_{\alpha r}\cdot\underline{P}_\alpha) \tag{3.51}$$

$$P_r = \sum_\alpha \frac{1}{\sqrt{m_\alpha}}\, \underline{\ell}_{\alpha r}\cdot\underline{P}_\alpha \tag{3.52}$$

$$\underline{p}_i = \underline{P}_i - \frac{m}{M}\Big(\sum_j \underline{P}_j + \sum_\alpha \underline{P}_\alpha\Big) \tag{3.53}$$

The above section is equivalent to starting with a Lagrangian of the form :

$$\mathcal{L} = \sum_{\lambda,\mu} \tfrac{1}{2} G^{\lambda\mu}\, \dot{q}_\lambda \dot{q}_\mu - V \tag{3.54}$$

where $q_\lambda$ is a generalised molecular coordinate, and obtaining the corresponding Hamiltonian :

$$\mathcal{H} = \sum_{\lambda,\mu} \tfrac{1}{2} G_{\lambda\mu}\, p_\lambda p_\mu + V \tag{3.55}$$

where $G_{\lambda\nu}$ is an element of the matrix inverse to that with elements $G^{\lambda\nu}$.

The complete Lagrangian (3.17) can be written in terms of these generalised molecular coordinates as :

$$\mathcal{L} = \sum_{\lambda,\nu} \tfrac{1}{2} G^{\lambda\nu} \dot{q}_\lambda \dot{q}_\nu - \sum_{\lambda} a_\lambda \dot{q}_\lambda - \sum_{\lambda,\nu} d_{\lambda\nu} \dot{q}_\lambda \dot{q}_\nu - \sum_{\lambda} b_\lambda \dot{q}_\lambda$$

$$- \sum_{\lambda,\nu,\eta,\xi} c_{\lambda\nu\eta\xi} \dot{q}_\lambda \dot{q}_\nu \dot{q}_\eta \dot{q}_\xi - V + 0(c^{-3}) \qquad (3.56)$$

where $a_\lambda$ is the external magnetic potential term of order $c^{-1}$, and the remaining coefficients are all of order $c^{-2}$; the terms d and c are symmetrical with respect to interchange of subscripts. The conjugate momentum is given by :

$$p_\lambda = \sum_{\nu} G^{\lambda\nu} \dot{q}_\nu - a_\lambda - b_\lambda - \sum_{\nu} 2d_{\lambda\nu} \dot{q}_\nu$$

$$- \sum_{\nu,\eta,\xi} 4c_{\lambda\nu\eta\xi} \dot{q}_\nu \dot{q}_\eta \dot{q}_\xi + 0(c^{-3}) \qquad (3.57)$$

This is equivalent to :

$$\dot{q}_\lambda = \sum_{\nu} G_{\lambda\nu} \Big\{ p_\nu + a_\nu + b_\nu + \sum_{\eta} 2d_{\nu\eta} \dot{q}_\eta$$

$$+ \sum_{\eta,\xi,\rho} 4c_{\nu\eta\xi\rho} \dot{q}_\eta \dot{q}_\xi \dot{q}_\rho \Big\} + 0(c^{-3}) \qquad (3.58)$$

The Hamiltonian is then given by :

$$\mathcal{H} = \sum_{\lambda} \frac{\partial \mathcal{L}}{\partial \dot{q}_{\lambda}} \dot{q}_{\lambda} - \mathcal{L}$$

$$= \sum_{\lambda} \tfrac{1}{2}(p_{\lambda} + a_{\lambda})\, \dot{q}_{\lambda} + \sum_{\lambda} \tfrac{1}{2} b_{\lambda} \dot{q}_{\lambda} - \sum_{\lambda,\nu,\eta,\xi} c_{\lambda\nu\eta\xi} \dot{q}_{\lambda} \dot{q}_{\nu} \dot{q}_{\eta} \dot{q}_{\xi} + V + O(c^{-3}) \qquad (3.59)$$

which on substitution of (3.58) gives :

$$\mathcal{H} = \sum_{\lambda,\nu} \tfrac{1}{2} G_{\lambda\nu}(p_{\lambda} + a_{\lambda})(p_{\nu} + a_{\nu}) + \sum_{\lambda} b_{\lambda} \dot{q}_{\lambda} + \sum_{\lambda,\nu} d_{\lambda\nu} \dot{q}_{\lambda} \dot{q}_{\nu}$$
$$+ \sum_{\lambda,\nu,\eta,\xi} c_{\lambda\nu\eta\xi} \dot{q}_{\lambda} \dot{q}_{\nu} \dot{q}_{\eta} \dot{q}_{\xi} + V + O(c^{-3}) \qquad (3.60)$$

All the latter terms in $q_{\lambda}$ are of order $c^{-2}$ and we can replace entirely by $p_{\nu}$ by substituting :

$$q_{\lambda} = \sum_{\nu} G_{\lambda\nu} (p_{\nu} + a_{\nu}) + O(c^{-2}) \qquad (3.61)$$

The elements $G_{\lambda\nu}$ that appear above are exactly identical to those obtained in the absence of external field effects, inter-particle interactions and relativistic corrections. Thus the complete Lagrangian (3.17) yields a molecular Hamiltonian :

$$\mathcal{H} = \frac{1}{2M}\pi^2 + \tfrac{1}{2}\underline{\Omega}\cdot\underline{\underline{\mu}}\cdot\underline{\Omega} + \sum_{r} \tfrac{1}{2}\Pi_r^2 + \sum_{i} \tfrac{1}{2}\Pi_i^2 + \frac{1}{2M_N}\Big(\sum_{i} \underline{\Pi}_i\Big)^2$$
$$+ \sum_{i} m\underline{B}_i \cdot \mathring{\dot{\underline{R}}}_i + \sum_{i} m^4 C \dot{R}_i^4 + \sum_{i,j} m^2 \mathring{\dot{\underline{R}}}_i \cdot \underline{\underline{D}}_{ij} \cdot \mathring{\dot{\underline{R}}}_j$$

$$+\sum_{i,\alpha} mm \ \underline{\dot{R}}_i \cdot \underline{\underline{D}}_{i\alpha} \cdot \underline{\dot{R}}_\alpha + \sum_\alpha m_\alpha \underline{B}_\alpha \cdot \underline{\dot{R}}_\alpha + V + O(c^{-3}) \tag{3.62}$$

where ,

$$\underline{\Pi} = \underline{P} + \underline{A} \tag{3.63}$$

$$\underline{\mathfrak{n}} = \underline{N} + \underline{A}_N \tag{3.64}$$

$$\Pi_r = P_r + A_r \tag{3.65}$$

and

$$\underline{\pi}_i = \underline{p}_i + \underline{a}_i \tag{3.66}$$

The A's are covariant quantities $^{21}$ and transform in the same way as the momenta. Thus $\underline{\Pi}, \underline{\mathfrak{n}}, \Pi_r$ and $\pi_i$ are related to $\underline{\Pi}_i$ and $\underline{\Pi}_\alpha$ in the same way as $\underline{P}$, $\underline{N}$, $P_r$ and $\underline{p}_i$ are related to $\underline{P}_i$ and $\underline{P}_\alpha$ (see equations (3.50) to (3.53) ). In (3.62), we have chosen to write the interaction terms of order $c^{-2}$ in terms of space-fixed velocities. This will aid the transformation to a quantum mechanical Hamiltonian.

It remains to express $\underline{\dot{R}}_i$ and $\underline{\mathring{R}}$ in terms of the new mechanical momenta :

$$\underline{\dot{R}}_i = \frac{1}{m} \underline{\Pi}_i + O(c^{-2}) \tag{3.67}$$

$$\underline{\mathring{R}} = \frac{1}{m_\alpha} \underline{\Pi}_\alpha + O(c^{-2}) \tag{3.68}$$

Then using the inverse of (3.50) to (3.53)

$$\underline{\dot{R}}_i = \frac{1}{m} \underline{\pi}_i + \frac{1}{M} \underline{\Pi} + O(c^{-2}) \tag{3.69}$$

$$\dot{\underline{R}}_\alpha = \frac{1}{M}\underline{\Pi} - \frac{1}{M_N}\sum_i \underline{\pi}_i + \sum_\alpha \frac{1}{\sqrt{m}_\alpha}\underline{\ell}_{\alpha r}\Pi_r$$

$$- \underline{r}^{\circ}_{\alpha}\wedge\underline{\underline{I}}''^{-1}\cdot\underline{\Omega} + O(c^{-2}) \qquad (3.70)$$

where $\underline{\underline{I}}''$ is related [26] to the tensor $\underline{\underline{\mu}}$ and $\underline{\underline{I}}^{\circ}$, the inertia tensor evaluated at the equilibrium positions of the nuclei, by :

$$\underline{\underline{\mu}} = \underline{\underline{I}}''^{-1}\,\underline{\underline{I}}^{\circ}\,\underline{\underline{I}}''^{-1} \qquad (3.71)$$

Strictly speaking, these small terms are the exact transform of the analogous small terms in (3.4). Also the kinetic energy terms are the exact transform of the space-fixed kinetic energy terms in a classical form.

## 3.4 Transformation to the Quantum Mechanical Hamiltonian

In the previous section, it was shown that the quantum mechanical Hamiltonian :

$$\mathcal{H} = \sum_i \frac{1}{2m}\pi_i^2 + \sum_\alpha \frac{1}{2m_\alpha}\Pi_\alpha^2 + V \qquad (3.72)$$

transforms into a molecule-fixed Hamiltonian with a classical form :

$$\mathcal{H} = \frac{1}{2M}\Pi^2 + \tfrac{1}{2}\underline{\Omega}\cdot\underline{\underline{\mu}}\cdot\underline{\Omega} + \tfrac{1}{2}\sum_r \Pi_r^2 + \frac{1}{2m}\sum_i \pi_i^2$$

$$+ \frac{1}{2M_N}\left(\sum_i \underline{\pi}_i\right)^2 + V \qquad (3.73)$$

The remaining terms of the total Hamiltonian can be obtained by direct substitution of momenta in a space system by those in the molecular system according to equations analogous to (3.70) and (3.71). It is thus necessary to find a way of transforming (3.73) to a quantum mechanical form.

An analogous problem has been considered by Wilson et al.[17-19]. They start off with a space-fixed Hamiltonian :

$$\mathcal{H} = \sum_{\alpha} \frac{1}{2m_{\alpha}} P_{\alpha}^{2} + V \tag{3.74}$$

This transforms to a classical molecular Hamiltonian of the form :

$$\mathcal{H} = \sum_{\lambda,\nu} \tfrac{1}{2}\, g_{\lambda\nu} p_{\lambda} p_{\nu} + V \tag{3.75}$$

Using the Podolsky transformation [22,19] for $\frac{\partial}{\partial q}$, the quantum mechanical form is :

$$\mathcal{H} = \sum_{\lambda,\nu} g^{\frac{1}{4}} p_{\lambda} g^{-\frac{1}{2}} g_{\lambda\nu} p_{\nu} g^{\frac{1}{4}} + V \tag{3.76}$$

where $g$ is the determinant of the matrix with elements $g_{\lambda\nu}$. (A proof of this is given in Appendix A). An exactly equivalent equation is obtained on the addition of electronic momenta. Let us first consider the field-free case, i.e. equation (3.48). The above manipulation cannot be performed directly on (3.48), since it involves $\underline{N}$ which is not a momentum conjugate to any given coordinates. Instead it has to be expressed first in terms of $p_{\theta}$, $p_{\phi}$, $p_{\chi}$ (conjugate to the Euler angle $\theta$, $\phi$, $\chi$) and the other conjugate momenta $P_r$ and $p_i$.

The basic argument has been given by Wilson, Decius and Cross [19] but will be included here for completeness. Initially we require the components of angular velocity in terms of $\dot{\theta}$, $\dot{\phi}$ and $\dot{\chi}$. These latter are true vector quantities and on compounding along the molecule x, y, z axes gives :

$$\begin{aligned}
\omega_x &= \dot{\theta}\sin\chi - \dot{\phi}\sin\theta\cos\chi \\
\omega_y &= \dot{\theta}\cos\chi + \dot{\phi}\sin\theta\sin\chi \\
\omega_z &= \dot{\phi}\cos\theta + \dot{\chi}
\end{aligned} \tag{3.77}$$

The inverse transformation is :

$$\begin{aligned}
\dot{\theta} &= \omega_x\sin\chi + \omega_y\cos\chi \\
\dot{\phi} &= -\omega_x\csc\theta\cos\chi + \omega_y\csc\theta\sin\chi \\
\dot{\chi} &= \omega_x\cot\theta\cos\chi - \omega_y\cot\theta\sin\chi + \omega_z
\end{aligned} \tag{3.78}$$

The components of total angular momentum are given by :

$$M_x = \frac{\partial T}{\partial\omega_x} = \frac{\partial\dot{\theta}}{\partial\omega_x}\cdot\frac{\partial T}{\partial\dot{\theta}} + \frac{\partial\dot{\phi}}{\partial\omega_x}\frac{\partial T}{\partial\dot{\phi}} + \frac{\partial\dot{\chi}}{\partial\omega_x}\frac{\partial T}{\partial\dot{\chi}} \tag{3.79}$$

$$= \sin\chi\, p_\theta - \csc\theta\cos\chi\, p_\phi + \cot\theta\cos\chi\, p_\chi \tag{3.80}$$

Then :

$$N_x = M_x - L_x - G_x$$

$$= \sin\chi \, p_\theta - \csc\theta \cos\chi \, p_\phi + \cot\theta \cos\chi \, p_\chi$$

$$- \sum_i (\underline{r}_i \wedge \underline{p}_i)_x - \sum_{r,s} \zeta^x_{rs} Q_r P_s \qquad (3.81)$$

Similarly,

$$N_y = \cos\chi \, p_\theta + \csc\theta \sin\chi \, p_\phi - \cot\theta \sin\chi \, p_\chi$$

$$- \sum_i (\underline{r}_i \wedge \underline{p}_i)_y - \sum_{r,s} \zeta^y_{rs} Q_r P_s \qquad (3.82)$$

$$N_z = p_\chi - \sum_i (\underline{r}_i \wedge \underline{p}_i)_z - \sum_{r,s} \zeta^z_{rs} Q_r P_s \qquad (3.83)$$

By a manipulation of the elements of the determinant of the g-matrix it is possible to remove all elements connecting rotation and vibration, rotation and electronic motion, and vibration and electronic motion on one side of the diagonal. Then :

$$g = \det g_{\lambda\nu}$$

$$= (\det \mu_{uv}) \operatorname{cosec}^2\theta \times (\text{mass dependent terms}) \qquad (3.84)$$

The "mass dependent terms" arise from the $1/m$ and $1/M_N$ terms in the electronic-electronic sub-matrix and is completely independent of all the coordinates. They all disappear on substitution into (3.76).

Thus writing $\mu$ as $\det \mu_{uv}$ :

$$= \sum_{\lambda,\nu} \tfrac{1}{2}\mu^{\frac{1}{4}}\sin^{-\frac{1}{2}}\theta \; p_\lambda \, \mu^{-\frac{1}{2}}\sin\theta \; g_{\lambda\nu} p_\nu \, \mu^{\frac{1}{4}}\sin^{-\frac{1}{2}}\theta \; + \; V \tag{3.85}$$

This is appropriate for an integration volume element $dq_1 dq_2 \cdots dq_n$, but it is customary to use a volume element $\sin\theta \, d\theta d\phi d\chi dQ_1 \cdots$.

This modifies the wave-function by a factor of $\sin^{\frac{1}{2}}\theta$ and the wave equation :

$$\mathcal{H}\psi = E\psi$$

corresponding to the Hamiltonian (3.85) should be replaced by :

$$\mathcal{H}'\psi' = E\psi'$$

where

$$\psi' = \sin^{-\frac{1}{2}}\theta \; \psi$$

$$\mathcal{H}' = \sum_{\lambda,\nu} \tfrac{1}{2}\mu^{\frac{1}{4}}\sin^{-1}\theta \; p_\lambda \, \mu^{-\frac{1}{2}}\sin\theta \; g_{\lambda\nu} p_\nu \, \mu^{\frac{1}{4}} \; + \; V \tag{3.86}$$

Then Wilson, Decius and Cross [19] show that after non-commutation properties have been taken into account, the Hamiltonian be written in terms of the original momenta (see (3.81) to (3.83) ) as :

$$\mathcal{H}' = \frac{1}{2M}P^2 + \sum_{u,v} \tfrac{1}{2}\mu^{\frac{1}{4}}(M_u - L_u - G_u)\mu^{-\frac{1}{2}}\mu_{uv}(M_v - L_v - G_v)\mu^{\frac{1}{4}}$$

$$+ \sum_r \mu^{\frac{1}{4}}p_r\mu^{-\frac{1}{2}}p_r\mu^{\frac{1}{4}} + \sum_i \frac{1}{2m}p_i^2 + \frac{1}{2M_N}\left(\sum_i p_i\right)^2 + V \tag{3.87}$$

This depends upon the fact that if the true momenta $p_\lambda$ are related to the ficticious momenta $M'_\nu$ by :

$$p_\lambda = \sum_\nu s_{\lambda\nu} M'_\nu \qquad M'_\lambda = \sum_\nu s^{\lambda\nu} p_\lambda \tag{3.88}$$

we require :

$$\det s_{\lambda\nu} = s = \sin\theta$$

and $$\sum_\lambda (p_\lambda s^{-1}) + \sum_{\lambda,\nu} s^{-1} s^{\lambda\nu} (p_\nu \sum_\rho s_{\rho\lambda}) = 0 \tag{3.89}$$

In the presence of fields the classical Hamiltonian becomes :

$$\mathcal{H} = \sum_{\lambda,\nu} \tfrac{1}{2} g_{\lambda\nu} \pi_\lambda \pi_\nu + V \tag{3.90}$$

But since $\pi_\lambda$ has the same transformation properties as $p_\lambda$ (they are both covariant quantities), the Podolsky transformation yields an equation similar to (3.86) i.e.

$$\mathcal{H}' = \sum_{\lambda,\nu} \tfrac{1}{2} \mu^{\frac{1}{4}} \sin^{-1}\theta\, \pi_\lambda \mu^{-\frac{1}{2}} \sin\theta\, g_{\lambda\nu} \pi_\nu \mu^{\frac{1}{4}} + V \tag{3.91}$$

This time we require :

$$(\sum_\lambda \pi_\lambda s^{-1}) + \sum_{\lambda,\nu} s^{-1} s^{\lambda\nu} (\pi_\nu \sum s_{\rho\lambda}) = 0 \tag{3.92}$$

But, $$\text{L.H.S.} = \sum_\lambda (p_\lambda s^{-1}) + \sum_{\lambda,\nu} s^{-1} s^{\lambda\nu} p_\nu (\sum_\rho s_{\rho\lambda})$$

$$= 0 \qquad \text{Q.E.D.}$$

Hence :

$$\mathcal{H}' = \frac{1}{2M}\Pi^2 + \sum_{u,v} \tfrac{1}{2}\mu^{\frac{1}{4}}\eta_u\mu^{-\frac{1}{2}}\mu_{uv}\eta_v\mu^{\frac{1}{4}} + \underset{i}{\ } \frac{1}{2m}\pi_i^2$$

$$+ \frac{1}{2M_N}\left(\sum_i \underline{\pi}_i\right)^2 + \sum_r \tfrac{1}{2}\mu^{\frac{1}{4}}\Pi_r\mu^{-\frac{1}{2}}\Pi_r\mu^{\frac{1}{4}} + V \qquad (3.93)$$

To this should be added the remaining terms from (3.9) :

$$\mathcal{H}'' = \mu^{-\frac{1}{4}}\left[\sum_i \left\{\underline{B}_i\cdot\underline{\Pi}_i + C\,\Pi_i^4 + \sum_j \underline{\Pi}_i\cdot\underline{\underline{D}}_{ij}\cdot\underline{\Pi}_j\right.\right.$$

$$\left.\left. + \sum_\alpha \underline{\Pi}_i\cdot\underline{\underline{D}}_{i\alpha}\cdot\underline{\Pi}_\alpha\right\} + \sum_\alpha \underline{B}_\alpha\cdot\underline{\Pi}_\alpha + V\right]\mu^{\frac{1}{4}} \qquad (3.94)$$

where $\underline{B}$, C and $\underline{\underline{D}}$ are given in (3.10) to (3.14) and $\underline{\Pi}_i$ and $\underline{\Pi}_\alpha$ are written in terms of molecular momenta as :

$$\underline{\Pi}_i = \underline{\pi}_i + \frac{m}{M}\underline{\Pi} \qquad (3.95)$$

$$\underline{\Pi}_\alpha = \frac{m_\alpha}{M}\underline{\Pi} - \frac{m_\alpha}{M_N}\sum_i \underline{\pi}_i + \sum_r \sqrt{m_\alpha}\,\underline{\ell}_{\alpha r}\Pi_r$$

$$- \sum_r \sqrt{m_\alpha}\,Q_r\underline{\ell}_{\alpha r}\wedge\underline{\underline{I}}''^{-1}\cdot\underline{\eta} \qquad (3.96)$$

## 3.5 Simplification of the Hamiltonian

In order to make use of the complete Hamiltonian (3.93) and (3.94) in physical problems, it is expedient to perform some further manipulations so that terms appear in a more familiar form. In doing this we shall frequently omit terms without comment if they make a negligible contribution to the energy; these terms are typically of order $c^{-3}$ or $(\frac{m}{M})^2 c^{-2}$ or higher.

Initially the space-fixed vector potentials are written in a form which satisfies a Coulomb gauge :

$$\underline{A}_i = \tfrac{1}{2}(\underline{H}\wedge\underline{R}_i) \; ; \qquad \underline{A}_\alpha = \tfrac{1}{2}(\underline{H}\wedge\underline{R}_\alpha) \tag{3.97}$$

Thus the molecule-fixed potentials, which are given by relationships similar to (3.52) to (3.53), are :

$$\begin{aligned}\underline{A} &= \frac{e}{c}\Big[\sum_i \underline{A}_i - \sum_\alpha Z_\alpha \underline{A}_\alpha\Big] \\ &= -\frac{e}{2c}\,\underline{H}\wedge\Big[q\underline{R} + \sum_\alpha Z_\alpha \underline{r}_\alpha - \big(1+\frac{mq}{M}\big)\sum_i \underline{r}_i\Big]\end{aligned} \tag{3.98}$$

$$\begin{aligned}\underline{A}_N &= \frac{e}{c}\sum_\alpha\Big[-Z_\alpha(\underline{r}_\alpha\wedge\underline{A}_\alpha) + \sum_{r,s}\frac{Z_\alpha}{\sqrt{m_\alpha}}\,\underline{\zeta}_{rs}Q_r(\underline{\ell}_{\alpha s}\cdot\underline{A}_\alpha)\Big] \\ &= -\frac{e}{2c}\sum_\alpha Z_\alpha\Big\{\underline{r}_\alpha\wedge\,\underline{H}\Big[\wedge\big(\underline{R}+\underline{r}_\alpha-\frac{m}{M}\sum_i\underline{r}_i\big)\Big] \\ &\qquad - \frac{1}{\sqrt{m_\alpha}}\sum_{r,s}\underline{\zeta}_{rs}Q_r\,\underline{\ell}_{\alpha s}\cdot\underline{H}\wedge\big(\underline{R}+\underline{r}_\alpha-\frac{m}{M}\sum_i\underline{r}_i\big)\Big\}\end{aligned} \tag{3.99}$$

$$\begin{aligned}A_r &= -\frac{e}{c}\sum_\alpha\frac{Z_\alpha}{\sqrt{m_\alpha}}\,\underline{\ell}_{\alpha r}\cdot\underline{A}_\alpha \\ &= -\frac{e}{2c}\sum_\alpha\frac{Z_\alpha}{\sqrt{m_\alpha}}\,\underline{\ell}_{\alpha r}\cdot\underline{H}\wedge\big(\underline{R}+\underline{r}_\alpha-\frac{m}{M}\sum_i\underline{r}_i\big)\end{aligned} \tag{3.100}$$

and

$$\begin{aligned}\underline{a}_i &= \frac{e}{c}\Big[\underline{A}_i - \frac{m}{M}\sum_j \underline{A}_j + \frac{m}{M}\sum_\alpha Z_\alpha \underline{A}_\alpha\Big] \\ &= \frac{e}{2c}\,\underline{H}\wedge\Big[\Big(1 + \frac{mq}{M}\Big)\underline{R} + \underline{r}_i - \Big(2 + \frac{mq}{M}\Big)\frac{m}{M}\sum_j \underline{r}_j + \frac{m}{M}\sum_\alpha Z_\alpha \underline{r}_\alpha\Big]\end{aligned} \tag{3.101}$$

In these equations the total molecular electric charge is :

$$q = \sum Z_\alpha - \sum_i 1 \tag{3.102}$$

and $\underline{R}_i$ and $\underline{R}_\alpha$ have been written in terms of molecular coordinates using equations (3.20) and (3.22). These potentials could be substituted directly into (3.87), but the presence of translational and vibrational coordinates in $\underline{a}_i$ is undesirable, since they lead to large second order effects in most representations of the total wave-function. However, these terms may be removed by a change of gauge [24,25], a suitable scalar function being :

$$F = \frac{e}{2c}\,\underline{H}\wedge\Big[\Big(1 + \frac{mq}{M}\Big)\underline{R} + \frac{m}{M}\sum_\alpha Z_\alpha \underline{r}_\alpha\Big]\cdot\Big[\sum_j \underline{r}_j\Big] \tag{3.103}$$

The total wave-function is multiplied by a phase factor exp $(iF/\hbar)$ and each potential $A_\lambda$ is replaced by $(A_\lambda - \frac{\partial F}{\partial q_\lambda})$. Thus

$$\underline{A} \longrightarrow \Big[-\frac{e}{2c}\,\underline{H}\wedge\Big[q\underline{R} + \sum Z_\alpha \underline{r}_\alpha - 2\Big(1 + \frac{mq}{M}\Big)\sum_i \underline{r}_i\Big] \tag{3.104}$$

$$A_r \longrightarrow -\frac{e}{2c}\sum_\alpha \frac{Z_\alpha}{\sqrt{m_\alpha}}\,\ell_{\alpha r}\cdot\underline{H}\wedge\Big(\underline{R} + \underline{r}_\alpha - 2\frac{m}{M}\sum_i \underline{r}_i\Big) \tag{3.105}$$

$$\underline{A}_N \rightarrow -\frac{e}{2c}\sum_{\alpha} Z_\alpha \Big\{ \underline{r}_\alpha \wedge \Big[ \underline{H} \wedge \big( \underline{R} + \underline{r}_\alpha - 2\frac{m}{M}\sum_{i} \underline{r}_i \big) \Big]$$

$$- \frac{1}{\sqrt{m_\alpha}} \sum_{r,s} \underline{\zeta}_{rs} Q_r \, \underline{\ell}_{\alpha s} \cdot \underline{H} \wedge \big( \underline{R} + \underline{r}_\alpha - 2\frac{m}{M} \sum_{i} \underline{r}_i \big) \Big\} \qquad (3.106)$$

and

$$\underline{a}_i \rightarrow \frac{e}{2c}\, \underline{H} \wedge \Big[ \underline{r}_i - \big(2 + \frac{mq}{M}\big) \frac{m}{M} \sum_{j} \underline{r}_j \Big] \qquad (3.107)$$

so that the latter contains only electron coordinates. Ideally one would like to obtain all potentials in forms involving only their corresponding coordinates, but this has not proved possible. However, the unwanted terms all give negligible contributions to the energy and will be omitted below; the Hamiltonian will then no longer be strictly gauge invariant, but this is permissible, since a definite gauge has now been chosen.

We shall now consider each term of (3.93,3.94) in turn, omitting all those contributions that are negligible in a separable representation of the form :

$$\Psi = \psi_{trans} \psi_{rot} \psi_{vib} \psi_{el} \,, \qquad (3.108)$$

where $\psi_{trans}$ is the translational wave-function and depends only on $\underline{R}$, the rotational wave-function, $\psi_{rot}$, depends only on the Euler angles associated with the orientation of the molecule, $\psi_{vib}$ is a function of the normal coordinates, $Q_r$, and the electronic wave-function depends on $\underline{r}_i$ and possibly $Q_r$.

The translational part, $\mathcal{H}_T$, of the Hamiltonian (3.93) is $\frac{1}{2M}(\underline{P} + \underline{A})^2$. Only those parts of $\underline{A}$ involving $\underline{R}$ give diagonal contributions, and the second order contributions of the other terms only connect different electronic and vibrational states and are therefore negligible except at very high fields. Thus :

$$\mathcal{H}_T = \frac{1}{2M} P^2 - \frac{qe}{2Mc} \underline{H}.(\underline{R}_\wedge \underline{P}) + \frac{q^2e^2}{8Mc^2} (\underline{H}_\wedge \underline{R})^2 \qquad (3.109)$$

and only adds to the energy a constant term that cannot be detected spectroscopically.

The rotational Hamiltonian can be expanded as :

$$\mathcal{H}_R = \sum_{u,v} \tfrac{1}{2}\mu^{\frac{1}{4}} N_u \mu_{uv} \mu^{-\frac{1}{2}} N_v \mu^{\frac{1}{4}} + \sum_{u,v} \tfrac{1}{2}\mu^{\frac{1}{4}} N_u \mu_{uv} A_{N_v} \mu^{-\frac{1}{4}}$$

$$\sum_{u,v} \tfrac{1}{2}\mu^{-\frac{1}{4}} A_{N_v} \mu_{uv} N_u \mu^{\frac{1}{4}} + \sum_{u,v} \tfrac{1}{2} A_{N_u} \mu_{uv} A_{N_v} \qquad (3.110)$$

Making use of the fact that :

$$\mu^{\frac{1}{4}}[\underline{N}, \mu^{-\frac{1}{4}}] + \mu^{-\frac{1}{4}}[\underline{N}, \mu^{\frac{1}{4}}] = [\underline{N}, \mu^{\frac{1}{4}}\mu^{-\frac{1}{4}}] = 0 \qquad (3.111)$$

the second and third terms of (3.110) become :

$$\sum_{u,v} \tfrac{1}{2} A_{N_v} \mu_{uv} N_u + \sum_{u,v} \tfrac{1}{2} N_u \mu_{uv} A_{N_v} \qquad (3.112)$$

In a similar way the vibrational part of the Hamiltonian is :

$$\mathcal{H}_V = \sum_r \tfrac{1}{2}\mu^{\frac{1}{4}}P_r\mu^{-\frac{1}{2}}P_r\mu^{\frac{1}{4}} + \sum_r \tfrac{1}{2}A_r^2 + \sum_r \tfrac{1}{2}\mu^{\frac{1}{4}}P_rA_r\mu^{-\frac{1}{4}} + \sum_r \tfrac{1}{2}\mu^{-\frac{1}{4}}A_rP_r\mu^{\frac{1}{4}} \qquad (3.113)$$

where the last two terms simplify to :

$$\sum_r A_rP_r + \tfrac{1}{2}\left[P_r, A_r\right] \qquad (3.114)$$

The second term in (3.114) can be shown to vanish by direct substitution (3.105) and (3.52). Now Watson[26] has shown that :

$$\sum_{u,v} \tfrac{1}{2}\mu^{\frac{1}{4}}N_u\mu_{uv}\mu^{-\frac{1}{2}}N_v\mu^{\frac{1}{4}} + \sum_r \tfrac{1}{2}\mu^{\frac{1}{4}}P_r\mu^{-\frac{1}{2}}P_r\mu^{\frac{1}{4}} = \sum_{u,v}\tfrac{1}{2}N_u\mu_{uv}N_v + \sum_r \tfrac{1}{2}P_r^2 - \frac{1}{8}\hbar^2\sum_u \mu_{uu} \qquad (3.115)$$

In addition it can be shown

$$\sum_v \mu_{uv}A_{N_v} = \sum_{\alpha,v} -\frac{Z_\alpha e}{c}\left(\underline{r}^o_\alpha \wedge \underline{A}_\alpha\right)_v \left(I''^{-1}\right)_{uv} \qquad (3.116)$$

where $\underline{\underline{I}}''$ is defined by (3.71). In addition $\underline{A}_\alpha$ is to be evaluated after the gauge transformation :

$$\underline{A}_\alpha = \tfrac{1}{2}\underline{H} \wedge \left(\underline{R} + \underline{r}_\alpha - 2\frac{m}{M}\sum_i \underline{r}_i\right) \qquad (3.117)$$

Addition of equations (3.110) and (3.113) and substitution of (3.105) (3.112) and (3.114) to (3.116) yields :

$$\mathcal{H}_R + \mathcal{H}_V = \sum_{u,v} \tfrac{1}{2} N_u \mu_{uv} N_v + \sum_{r} \tfrac{1}{2} P_r^2 - \frac{1}{8} \hbar^2 \sum_{u} \mu_{uu} + \sum_{r} \tfrac{1}{2} A_r^2$$

$$+ \sum_{,u,v} - \frac{Z_\alpha e}{2c} \left[ (\underline{r}^o_\alpha \wedge \underline{A}_\alpha)_v (I''^{-1})_{uv} N_u + N_u (\underline{r}^o_\alpha \wedge \underline{A})_v (I''^{-1})_{uv} \right]$$

$$+ \sum_{,r} - \frac{Z_\alpha e}{\sqrt{m_\alpha} c} (\underline{\ell}_{\alpha r} \cdot \underline{A}_\alpha) P_r + \sum_{u,v} \tfrac{1}{2} A_{N_v} \mu_{uv} A_{N_v} \qquad (3.118)$$

In substituting (3.117) for $\underline{A}_\alpha$, terms involving translational and electronic coordinates may be omitted since they are negligible. In equation (3.119) the first three terms are, respectively, the rotational kinetic energy, the vibrational kinetic energy and the mass-dependent contribution to the potential energy that has been discussed by Watson [26]. The next and last terms are responsible for rotational and vibrational contributions to diamagnetism. The remaining two terms are linear in external magnetic field and represent rotational and vibrational Zeeman effects.

The electronic part of the Hamiltonian is :

$$\mathcal{H}_e = \frac{1}{2m} \sum_i (\underline{p}_i + \underline{a}_i)^2 + \frac{1}{2M_N} \left[ \sum_i (\underline{p}_i + \underline{a}_i) \right]^2 - \frac{1}{8m^3c^2} \sum_i \Pi_i^4 \qquad (3.119)$$

Substituting equation (3.107) for $\underline{a}_i$ and neglecting small terms this becomes :

$$\mathcal{H}_e = \frac{1}{2m} \sum_i p_i^2 + \frac{1}{2M_N} \left( \sum_i \underline{p}_i \right)^2 - \frac{1}{8m^3c^2} \sum_i p_i^4$$

$$+ \frac{e}{2mc}\sum_{i} \underline{H}\cdot\left[\underline{r}_i\left(1 - \frac{m}{M}\right) - \frac{m}{M}\sum_{j\neq i}\underline{r}_j\right]\wedge \underline{p}_i$$

$$- \frac{e}{4m^3c^3}\sum_{i} \underline{H}\cdot(\underline{r}_i\wedge\underline{p}_i)p_i^2 + \frac{e^2}{2mc^2}\sum_{i} A_i^2 \qquad (3.120)$$

The first three terms are the kinetic energy of the electrons together with the mass-polarization and relativistic corrections; the next terms represent the electronic orbital Zeeman interaction also with its mass-polarization and relativistic corrections, while the final term is responsible for electron diamagnetism.

The remaining terms of the Hamiltonian (3.94) may be considered in four parts, the first being :

$$\mathcal{H}_1 = \sum_{i} \underline{B}_i\cdot\underline{\Pi}_i$$

$$= \frac{g\beta e}{2mc}\sum_{i}\sum_{j\neq i}\frac{1}{r_{ij}^3}\,\underline{s}_i\cdot(2\underline{r}_{ij}\wedge\underline{p}_j - \underline{r}_{ij}\wedge\underline{p}_i) + \sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}^3}\,\underline{s}_i\cdot(\underline{r}_{i\alpha}\wedge\underline{p}_i)\Big]$$

$$+ \sum_{i,\alpha}\frac{g_\alpha\beta_N e}{mc}\frac{1}{r_{i\alpha}^3}\,\underline{I}_\alpha\cdot(\underline{r}_{i\alpha}\wedge\underline{p}_i) + \sum_{i}\frac{g\beta}{2mc}\,\underline{s}_i\cdot(\underline{E}\wedge\underline{p}_i) \qquad (3.121)$$

The first two terms give the spin-orbit and spin-other-orbit interactions, while the third term represents the interaction of the nuclear spins with the electronic orbital angular momentum. The last term gives the interaction of the moving electrons with the static electric field, and is usually negligible as are the magnetic field (gauge invariance) terms which have been omitted.

Using equation (3.96) we have :

$$
\begin{aligned}
\mathcal{H}_2 &= \sum_{\alpha} \mu^{-\frac{1}{4}} \underline{B}_{\alpha} \cdot \underline{\Pi}_{\alpha} \mu^{\frac{1}{4}} \\
&= \sum_{\alpha,i,j} \frac{Z_{\alpha} g\beta e}{M_N c} \frac{1}{r_{i\alpha}^3} \underline{s}_i \cdot (\underline{r}_{i\alpha} \wedge \underline{p}_j) \\
&\quad + \sum_{\alpha,i,r} - \frac{Z_{\alpha} g\beta e}{\sqrt{m_{\alpha}} c} \frac{1}{r_{i\alpha}^3} I''^{\frac{1}{2}} \underline{s}_i \cdot (\underline{r}_{i\alpha} \wedge \underline{\ell}_{\alpha r}) P_r I''^{-\frac{1}{2}} \\
&\quad + \sum_{\alpha,i} \frac{Z_{\alpha} g\beta e}{c} \frac{1}{r_{i\alpha}^3} I''^{\frac{1}{2}} \underline{s}_i \cdot \underline{r}_{i\alpha} \wedge (\underline{r}_{\alpha}^{0} \wedge \underline{\underline{I}}''^{-1} \cdot \underline{N}) I''^{-\frac{1}{2}} \qquad (3.122)
\end{aligned}
$$

where the three terms represent, respectively, the mass polarization correction to the spin-orbit and spin-other-orbit coupling, the spin-vibration interaction and the spin-rotation interaction.

The third of the remaining terms is :

$$
\begin{aligned}
\mathcal{H}_3 &= \sum_{i,j} \underline{\Pi}_i \cdot \underline{D}_{ij} \cdot \underline{\Pi}_j \\
&= - \sum_{i} \sum_{j \neq i} \frac{e^2}{4m^2 c^2} \underline{p}_i \cdot \left(\frac{1}{r_{ij}} + \underline{r}_{ij} \frac{1}{r_{ij}^3} \underline{r}_{ij}\right) \cdot \underline{p}_j \\
&\quad - \sum_{i} \frac{g\beta}{2m^2 c^2} (\underline{s}_i \cdot \underline{H}) p_i^2 \qquad (3.123)
\end{aligned}
$$

and gives the retarded interaction between moving electrons (orbit-orbit interaction) and the relativistic correction to the electron spin Zeeman term which appears in V (see equation (3.8) ). Finally :

$$\begin{aligned}\mathcal{H}_4 &= \sum_{i,\alpha} \mu^{-\frac{1}{4}} \underline{\Pi}_i \cdot \underline{D}_{i\alpha} \cdot \underline{\Pi}_\alpha \mu^{\frac{1}{4}} \\ &= -\sum_{\alpha,i,j} \frac{Z_\alpha e^2}{2mM_N c^2} \underline{p}_i \cdot \left(\frac{1}{r_{i\alpha}} + \underline{r}_{i\alpha} \frac{1}{r_{i\alpha}^3} \underline{r}_{i\alpha}\right) \cdot \underline{p}_j \\ &\quad + \sum_{\alpha,i} \frac{Z_\alpha e^2}{2m\sqrt{m_\alpha} c^2} I''^{\frac{1}{2}} \underline{p}_i \cdot \left(\frac{1}{r_{i\alpha}} + \underline{r}_{i\alpha} \frac{1}{r_{i\alpha}^3} \underline{r}_{i\alpha}\right) \cdot \left(\sum_r \underline{\ell}_{\alpha r} P_r\right) I''^{-\frac{1}{2}} \\ &\quad - \sum_{\alpha,i} \frac{Z_\alpha e^2}{2mc^2} I''^{\frac{1}{2}} \underline{p}_i \cdot \left(\frac{1}{r_{i\alpha}} + \underline{r}_{i\alpha} \frac{1}{r_{i\alpha}^3} \underline{r}_{i\alpha}\right) \cdot \left(\underline{r}_\alpha^0 \wedge \underline{I}''^{-1} \cdot \underline{N}\right) I''^{-\frac{1}{2}}\end{aligned} \tag{3.124}$$

These are respectively the mass polarization correction to the orbit-orbit interaction of (3.123), the orbit-vibration and the orbit-rotation interactions.

The expression for the potential energy, V, is the same as that given in equation (3.8), but with each interparticle distance $\underline{R}_{\lambda\nu}$ replaced by $\underline{r}_{\lambda\nu}$.

Equations (3.109), (3.118), (3.120 to 124) and (3.8) together give a complete Hamiltonian (correct to order $c^{-2}$) for a non-linear molecule in the presence of constant electromagnetic fields. In this Hamiltonian are several new terms which have only been investigated in simple systems like atoms. These new terms include mass-polarization corrections to the orbital Zeeman interaction (3.120), the spin-orbit coupling (3.122), and the orbit-orbit interaction (3.124). The first of these has been considered by Abragam and Van Vleck [11] in the case of the oxygen atom. They may be important in considering the effects of isotopic substitution on spectra and, since they are proportional to (m/M), their relative importance will be greatest for light species; however, the spin-orbit correction will have the largest magnitude for molecules with heavy nuclei.

Other novel terms are the spin-vibration interaction (3.122) and the orbit-vibration interaction (3.124), which however only give diagonal contributions if the molecule has sufficient symmetry for some of the vibrational modes to be degenerate; this is related to the fact that $\underline{\zeta}_{rs}Q_rP_s$ only contributes in first order if r and s are two components of a degenerate mode.

Equation (3.118) includes a vibration as well as a rotational Zeeman term. This would modify the g-factor of a molecule (whether closed- or open- shell), when it is in a degenerate vibrational state (a degenerate mode has been excited), but to the author's knowledge such an effect has not yet been observed.

## 3.6 Quantum Mechanical Hamiltonian for a Linear Molecule

The Hamiltonian derived so far is only strictly valid for non-linear molecules. The modifications that have to be made for linear molecules will be outlined in the following section.

The derivation of the classical Hamiltonian is exactly analogous to that given for a general non-linear molecule in Section 3.3, except that the Eckart equation (3.30) only gives two conditions specifying the molecule-fixed axis system. This is equivalent to the idea that a linear molecule has only two degrees of rotational freedom, i.e. its orientation is specified by just two Euler angles $\theta$ and $\phi$. For an n-atom molecule, there are consequently (3n-5) instead of (3n-6) vibrational degrees of freedom. Throughout, we shall take the figure axis of the linear molecule to be the z axis. The equilibrium positions of the nuclei are $\underline{a}_\alpha$ (situated on the z axis). Then the Eckart conditions are :

$$\sum_\alpha m_\alpha \underline{a}_\alpha \wedge \underline{r}_\alpha = 0 \qquad (3.125)$$

and the vibrational normal coordinates are defined by :

$$\sqrt{m_\alpha}(\underline{r}_\alpha - \underline{a}_\alpha) = \sum_r \underline{\ell}_{\alpha r} Q_r \qquad (3.126)$$

The new orthogonality relationships for the components of $\underline{\ell}_{\alpha r}$ are given by Amat and Henry [29].

The derivation of conjugate momenta is exactly the same as in (3.38) to (3.43) except now :

$$I'_{xy} = I'_{xz} = I'_{yz} = I'_{zz} = 0 \tag{3.127}$$

$$I'_{xx} = I'_{yy} = I' \text{ , say} \tag{3.128}$$

where,

$$I' = \frac{1}{I_e}\left( I_e + \sum_r \tfrac{1}{2}\bar{a}_r Q_r \right)^2 \tag{3.129}$$

The proof of these is given by Amat and Henry [29] and also Watson [30]. Also , $I_e$ is the value of I' at the equilibrium configuration.

$$I_e = \sum_\alpha m_\alpha a_\alpha^2 \tag{3.130}$$

$$\bar{a}_r = \sum_\alpha 2\sqrt{m_\alpha}\, a_\alpha\, \ell_{\alpha r}^{z} \tag{3.131}$$

$$I' = \frac{I^2}{I_e} \tag{3.132}$$

with

$$I = \sum_\alpha m_\alpha z_\alpha^2 \tag{3.133}$$

Therefore :

$$\begin{aligned} J_x - L_x - G_x &= I'\omega_x \\ J_y - L_y - G_y &= I'\omega_y \end{aligned} \tag{3.134}$$

$$J_z - L_z - G_z = 0 \tag{3.135}$$

Inverting (3.134), we obtain :

$$\omega_x = \frac{1}{I'}(J_x - L_x - G_x) \; ; \quad \omega_y = \frac{1}{I'}(J_y - L_y - G_y) \qquad (3.136)$$

The Lagrangian equivalent to (3.48) is :

$$2\mathcal{L} = \omega_x J_x + \omega_y J_y + \sum_r P_r \dot{Q}_r + \sum_i \underline{p}_i \cdot \dot{\underline{r}}_i + \frac{P^2}{M} - 2V \qquad (3.137)$$

Then if we replace $\frac{1}{2I'}$ by B, the classical molecular Hamiltonian becomes :

$$\mathcal{H} = \frac{P^2}{2M} + B\,(J_x - G_x - L_x)^2 + (J_y - G_Y - L_y)^2 + \sum_r \tfrac{1}{2}P_r^2 + \frac{1}{2m}\sum_i p_i^2 + \frac{1}{2M_N}\left(\sum_i \underline{p}_i\right)^2 + V \qquad (3.138)$$

It is now necessary to transform to quantum mechanical form; the method of Wilson, Decius and Cross [19] cannot be used without modification because of the lack of the third Euler angle. It is still, however, necessary to write the components of $\underline{N}$ $(=\underline{J}-\underline{G}-\underline{L})$ in terms of $p_\theta$, $p_\phi$, $P_r$ and $\underline{p}_i$. The angular velocities are given by:

$$\begin{aligned} \omega_x &= -\dot{\phi}\sin\theta \\ \omega_y &= \dot{\theta} \\ \omega_z &= \dot{\phi}\cos\theta \end{aligned} \qquad (3.139)$$

The inverse transformation, however, is not unique :

$$\dot{\theta} = \omega_y$$

$$\dot{\phi} = -\omega_x \operatorname{cosec}\theta \text{ or } \omega_z \sec\theta \text{ or combinations.} \qquad (3.140)$$

From (3.139) :

$$p_\theta = \frac{\partial T}{\partial \dot{\theta}} = \frac{\partial T}{\partial \omega_x}\frac{\partial \omega_x}{\partial \dot{\theta}} + \frac{\partial T}{\partial \omega_y}\frac{\partial \omega_y}{\partial \dot{\theta}} + \frac{\partial T}{\partial \omega_z}\frac{\partial \omega_z}{\partial \dot{\theta}}$$

$$= \mathcal{J}_y \qquad (3.141)$$

Here $\underline{J}$ has been replaced by $\underline{\mathcal{J}}$ to emphasise the point that its components do not obey commutation relations for angular momenta.

Similarly :

$$p_\phi = -\mathcal{J}_x \sin\theta + \mathcal{J}_z \cos\theta \qquad (3.142)$$

It is not possible to write $\mathcal{J}_x$ in terms of $p_\phi$, but using (3.135) :

$$\mathcal{J}_z = \sum_i (\underline{r}_i \wedge \underline{p}_i)_z + \sum_{r,s} \zeta^z_{rs} Q_r P_s \qquad (3.143)$$

and

$$\mathcal{J}_x = -p_\phi \operatorname{cosec}\theta + \cot\theta \sum_i (\underline{r}_i \wedge \underline{p}_i)_z + \sum_{r,s} \zeta^z_{rs} Q_r P_s \qquad (3.144)$$

The classical Hamiltonian has the form :

$$\mathcal{H} = \sum_{\mu,\nu} \tfrac{1}{2} M'_\mu G_{\mu\nu} M'_\nu + V \qquad (3.145)$$

where the $M'_\mu$ are related to the conjugate momenta by :

$$M'_{\mu} = \sum_{\nu} s^{\mu\nu} p_{\nu}$$

where $s^{\mu\nu}$ is the symmetric matrix defining the transformation. This yields :

$$\mathcal{H} = \sum_{\mu,\nu} \tfrac{1}{2} p_{\mu}\, g_{\mu\nu}\, p_{\nu} + V \tag{3.146}$$

After the Podolsky transformation [22,23] (also Appendix A), the quantum mechanical form is :

$$\begin{aligned} \mathcal{H} &= \sum_{\mu,\nu} \tfrac{1}{2} g^{\frac{1}{4}} p_{\mu} g^{-\frac{1}{2}} g_{\mu\nu} p_{\nu} g^{\frac{1}{4}} + V \\ &= \sum_{\mu,\nu} \tfrac{1}{2} g^{\frac{1}{4}} \tilde{M}'_{\mu} g^{-\frac{1}{2}} G_{\mu\nu} M'_{\nu} g^{\frac{1}{4}} + V \end{aligned} \tag{3.147}$$

where the quantum mechanical operator :

$$\tilde{M}'_{\mu} = \sum_{\nu} p_{\nu}\, s^{\mu\nu} \tag{3.148}$$

However, for linear molecules $p_{\nu}$ and $s^{\mu\nu}$ commute; therefore $\tilde{M}'_{\mu}$ can be replaced by $M'_{\mu}$ in (3.147).

The determinant $g$ of $g_{\mu\nu}$ is :

$$g = K' \frac{1}{I'^2} \operatorname{cosec}^2\theta = KB^2 \operatorname{cosec}^2\theta \tag{3.149}$$

where $K'$ and $K$ are functions of only the masses of the particles. Equation (3.147) applies when one has a weight factor of unity in the normalisation of the wave-function. Using the more usual weight factor of $\sin\theta$ , the Hamiltonian should be pre-multiplied by $\sin^{-\frac{1}{2}}\theta$ and post-multiplied by $\sin^{\frac{1}{2}}\theta$ ; yielding :

$$\mathcal{H} = \frac{P^2}{2M} + B(N_x^2 + \operatorname{cosec}\theta\, N_y \sin\theta\, N_y) + \sum_r \tfrac{1}{2}B^{\frac{1}{2}}P_r B^{-1} P_r B^{\frac{1}{2}} + \sum_i \frac{1}{2m}\, p_i^2 + \frac{1}{2M_N}\Big(\sum_i \underline{p}_i\Big)^2 + V \qquad (3.150)$$

Expanding the rotational terms and putting the total internal angular momentum, $\underline{W} = \underline{G} + \underline{L}$, we obtain :

$$B(N_x^2 + \operatorname{cosec}\theta\, N_y \sin\theta\, N_y)$$

$$= B\big[\mathcal{J}_x^2 + \operatorname{cosec}\theta\, \mathcal{J}_y \sin\theta\, \mathcal{J}_y - W_x\mathcal{J}_x - \mathcal{J}_x W_x - \operatorname{cosec}\theta\, \mathcal{J}_y \sin\theta\, W_y - W_y\mathcal{J}_y + W_x^2 + W_y^2\big] \qquad (3.151)$$

This is equal to the expression given by Hougan for the case of the linear triatomic molecule [31] after making use of the non-commutation properties of $\underline{\mathcal{J}}$ with $\underline{W}$ and $\sin\theta$.

$$\mathcal{H}_R = B(\mathcal{J}_x^2 + \operatorname{cosec}\theta\, \mathcal{J}_y \sin\theta\, \mathcal{J}_y - 2W_x\mathcal{J}_x - 2W_y\mathcal{J}_y + W_x^2 + W_y^2) \qquad (3.152)$$

The same author has shown that the above Hamiltonian (3.152) is isomorphic with a symmetric-top Hamiltonian, where the third Euler angle $\chi$ is introduced. This form is more suitable, since then the techniques of spherical tensor operators (to be described in the next chapter) can be used in evaluating matrix elements. Here we obtain the same result by means of a similarity transformation.

$$\text{i.e. } \mathcal{H} \longrightarrow S\mathcal{H}S^{-1} \quad \text{and} \quad \psi \longrightarrow S\psi \tag{3.153}$$

If S is taken to be exp $(iW_z\chi/\hbar)$, the rotational wave-function automatically takes on the form of a symmetric top wave-function. It is also an eigenfunction of the operator $p_\chi = -i\hbar\frac{\partial}{\partial\chi}$, with eigenvalues equal to those of $W_z$. Therefore it is possible to replace $W_z$ by $p_\chi$ whenever it acts directly on the wave-function. Elsewhere $W_z$ can be replaced by $p_\chi$ if the commutation properties with other terms in the expression are taken into account.

Now the effect of the similarity transformation on the various terms in the Hamiltonian is as follows.

$$\exp(iW_z\chi/\hbar)\, G_x \exp(-iW_z\chi/\hbar)$$

$$= \exp(iG_z\chi/\hbar)\, G_x \exp(-iG_z\chi/\hbar)$$

$$= \sum_{s=0}^{\infty} \frac{(-i)^s\chi^s}{s!\hbar^s}\left[\cdot\left[\left[\left[G_x, G_z\right], G_z\right], G_z\right]\cdots\cdots\right] \tag{3.154}$$

where there are s commutators. Also Watson has shown [26,30] that :

$$\begin{aligned} \left[G_x\, ,\, G_z\right] &= -i\hbar G_y \\ \left[G_y\, ,\, G_z\right] &= i\hbar G_x \end{aligned} \tag{3.155}$$

Therefore,

$$S\,G_x\,S^{-1} = \sum_{s\ \text{even}} (-1)^{s/2} \frac{\chi^s}{s!} G_x + \sum_{s\ \text{odd}} (-1)^{(s+1)/2} \frac{\chi^s}{s!} G_y$$

$$= G_x \cos\chi - G_y \sin\chi \qquad (3.156)$$

Similarly

$$S\,G_y\,S^{-1} = G_y \cos\chi + G_x \sin\chi \qquad (3.157)$$

The physical interpretation of the operator S is a rotation of the physical system by an angle $-\chi$ about the molecule-fixed z-axis or a positive rotation of the axes by $\chi$ about the same axis. We shall use the latter definition because it leaves the Euler angles specifying the molecular axis system as $(\phi,\theta,\chi)$ as required. The effect of the similarity transformation on an operator $F(\alpha)$ where $\alpha$ represents the point at which it is operating,

$$S\,F(\alpha)\,S^{-1} = F'(\alpha) = F(\alpha') \qquad (3.158)$$

can be interpretated as follows. Initially we have F operating at point $\alpha$ in the original axis system. After the rotation, at the point $\alpha$ in the new axis system the operator is a different function $F'$ of the position coordinates. However this is identical to the original operator with different arguements $\alpha'$; these correspond to the coordinates of the new point (in the original axis system) which have coordinates $\alpha$ in the new axis system.

The same is true with differential operators,

$$S\,G_x\,S^{-1} = G_x' = G_x\cos\chi - G_y\sin\chi \qquad (3.156')$$

$G_x$ and $G_y$ have definite operator forms in whichever system they are measured and the effect of the similarity transformation is to alter the point of operation of $G_x$ to a new point where the operator becomes $G_x'$ (i.e. the same operator except that the original coordinates are replaced by the new coordinates obtained after a rotation by $\chi$ about the molecular z-axis). It can be rewritten in terms of the original arguements or coordinates, which may be considered as those in the new axis system; $G_x$ and $G_y$ on the right hand side of (3.156) are operators in the new axis system.

Similarly,

$$S\,L_x\,S^{-1} = L_x\cos\chi - L_y\sin\chi \qquad (3.159)$$

$$S\,L_y\,S^{-1} = L_y\cos\chi + L_x\sin\chi \qquad (3.160)$$

Similar results are obtained for the position coordinates:

$$S\,x_\lambda\,S^{-1} = x_\lambda\cos\chi - y_\lambda\sin\chi \qquad (3.161)$$

$$S\,y_\lambda\,S^{-1} = y_\lambda\cos\chi + x_\lambda\sin\chi \qquad (3.162)$$

for $\lambda = \alpha$ or i.

The problem with vibrational coordinates and momenta is more complicated. If a vibration is non-degenerate, that is, it is one along the z-axis, its normal coordinates and momenta are left unchanged by the similarity transformation. The remaining doubly-degenerate modes, in the x,y plane can be expressed in terms of their x and y components, $P_r^x$ or $Q_r^x$ etc.

$$S P_r^x S^{-1} = P_r^x \cos\chi - P_r^y \sin\chi \qquad (3.163)$$

$$S P_r^y S^{-1} = P_r^y \cos\chi + P_r^x \sin\chi \qquad (3.164)$$

$$S Q_r^x S^{-1} = Q_r^x \cos\chi - Q_r^y \sin\chi \qquad (3.165)$$

$$S Q_r^y S^{-1} = Q_r^y \cos\chi + Q_r^x \sin\chi \qquad (3.166)$$

It is found convenient to rewrite $\mathcal{J}_x$ and $\mathcal{J}_y$ in terms of the components along the new x and y axes.

$$\mathcal{J}_x = J_x' \cos\chi - J_y' \sin\chi \qquad (3.167)$$

$$\mathcal{J}_y = J_y' \cos\chi + J_x' \sin\chi \qquad (3.168)$$

where the components of $\underline{J}'$ are defined by :

$$J_x' = \cos\chi(\cot\theta\, W_z - \operatorname{cosec}\theta\, p_\phi) + \sin\chi\, p_\theta \qquad (3.169)$$

$$J_y' = -\sin\chi(\cot\theta\, W_z - \operatorname{cosec}\theta\, p_\phi) + \cos\chi\, p_\theta \qquad (3.170)$$

$$J_z' = W_z \qquad (3.171)$$

These are readily related to the true rotational angular momentum $J_x, J_y$ and $J_z$ given in (3.79) to (3.83) by replacing $W_z$ by $p_\chi$. The rotational Hamiltonian (3.151) then becomes :

$$\mathcal{H}_R = B \operatorname{cosec}\theta\,(J_x' - W_x)\,\sin\theta\,(J_x' - W_x) + B \operatorname{cosec}\theta\,(J_y' - W_y)\,\sin\theta\,(J_y' - W_y) \tag{3.172}$$

$$= B\left[(J_x' - W_x)^2 + (J_y' - W_y)^2\right] - i\hbar\, B \cot\theta\,\left[\sin\chi\,(J_x' - W_x) + \cos\chi\,(J_y' - W_y)\right]$$

But,

$$\begin{aligned} W_z(J_x' - W_x) &= W_z\,(J_x - W_x) \\ &= (J_x - W_x)\,W_z - i\hbar\, W_y \\ &= p_\chi\,(J_x - W_x) + i\hbar\,(J_y - W_y) \end{aligned} \tag{3.173}$$

Similarly,

$$W_z(J_y' - W_y) = p_\chi\,(J_y - W_y) - i\hbar\,(J_x - W_x) \tag{3.174}$$

Using these above relationships and replacing $\underline{J}'$ by $\underline{J}$ in (3.172) gives :

$$\mathcal{H}_R = B\left[(J_x - G_x - L_x)^2 + (J_y - G_y - L_y)^2\right] \tag{3.175}$$

$$= B\,(\underline{J} - \underline{G} - \underline{L})^2 \tag{3.176}$$

since,

$$(J_z - G_z - L_z)^2 = (J_z' - G_z - L_z)^2 = 0 \tag{3.177}$$

All the remaining terms in the Hamiltonian are unchanged in form after the similarity transformation.

Now in the presence of external fields, the quantum mechanical Hamiltonian equivalent to (3.150) is :

$$\mathcal{H} = \frac{\Pi^2}{2M} + B\,\Pi_x^2 + B\operatorname{cosec}\theta\,\Pi_y \sin\theta\,\Pi_y + \sum_r \tfrac{1}{2}B^{\frac{1}{2}}\,\Pi_r B^{-1}\,\Pi_r B^{\frac{1}{2}}$$

$$+ \sum_i \frac{1}{2m}\pi_i^2 + \frac{1}{2M_N}\Big(\sum_i \underline{\pi}_i\Big)^2 + V \qquad (3.178)$$

We shall now perform the similarity transformation on the complete Hamiltonian, but the effect on the vector potential terms is slightly different. First, it will be assumed that all the potentials have been gauge transformed as in equations (3.104) to (3.107). Also it will be assumed that only those coordinates which appear in their corresponding vector potentials give non-negligible contributions; this is the same assumption as that made for the general molecule and which is found to be true for fields up to tens of kilogauss. Then we obtain :

$$\underline{A} = -\frac{e}{2c}\,\underline{H}\wedge q\underline{R} \qquad (3.179)$$

$$\underline{A}_N = -\frac{e}{2c}\,I''\,I^{0-1}\sum_\alpha Z_\alpha \underline{r}^0_\alpha \wedge (\underline{H}\wedge \underline{r}_\alpha) \qquad (3.180)$$

yielding $(A_N)_z = 0$, as expected by analogy with $N_z = 0$,

$$A_r = -\frac{e}{2c} \sum_{\alpha} \frac{Z_\alpha}{\sqrt{m_\alpha}} \underline{\ell}_{\alpha r} \cdot (\underline{H} \wedge \underline{r}_\alpha) \tag{3.181}$$

$$\underline{a}_i = \frac{e}{2c} \underline{H} \wedge \left[ \underline{r}_i - \left(2 + \frac{mq}{M}\right) \frac{m}{M} \sum_j \underline{r}_j \right] \tag{3.182}$$

The magnetic field, $\underline{H}$, is unchanged by the similarity transformation; this is because it is assumed to be a constant, independent of coordinates and momenta,

$$\text{i.e.} \quad S\, H_x\, S^{-1} = H_x \tag{3.183}$$

The subscripts are somewhat misleading, because here the result is a field component along the original axes (but acting at the new point $x', y'$). If we want the components along the new axes, we have to perform a transformation of axes along which the field is resolved. Therefore :

$$H_x = H_x^* \cos \chi - H_y^* \sin \chi \tag{3.184}$$

$$H_y = H_y^* \cos \chi + H_x^* \sin \chi \tag{3.185}$$

where asterisks have been added to the components in the new axis system for clarity; but they will be dropped later when no confusion can arise. Thus the rotational vector potentials transform as:

$$S\, (A_N)_x\, S^{-1} = (A_N^*)_x \cos \chi - (A_N^*)_y \sin \chi \tag{3.186}$$

$$S\, (A_N)_y\, S^{-1} = (A_N^*)_y \cos \chi + (A_N^*)_x \sin \chi \tag{3.187}$$

where the resulting vector potentials $\underline{A}^*$ are measured at point $x,y$ in the rotated axis system.

The cross terms between rotational angular momentum and field transform to :

$$\mathcal{H}_{RZ} = B\left[\cos\theta\,(J_x' - W_x) - \sin\chi\,(J_y' - W_y)\right]\left[(A_N^*)_x \cos\chi - (A_N^*)_y \sin\chi\right]$$

$$+ B \operatorname{cosec}\theta\left[(J_x' - W_x)\sin\chi + (J_y' - W_y)\cos\chi\right]\sin\theta$$

$$\times\left[(A_N^*)_x \sin\chi + (A_N^*)_y \cos\chi\right] + B\,\underline{A}_N^*.(\underline{J}' - \underline{W}) \qquad (3.188)$$

Bringing the $\sin\theta$ to the front, the above expression becomes :

$$\mathcal{H}_{RZ} = B\,(\underline{J}' - \underline{W}).\,\underline{A}_N^* + B\,\underline{A}_N^*.(\underline{J}' - \underline{W})$$

$$- \;ih\cot\theta\left\{(A_N^*)_x \sin\chi + (A_N^*)_y \cos\chi\right\} \qquad (3.189)$$

It is now desirable to replace the operator $W_z$ in $\underline{J}'$ by $p_\chi$. The relevant part of (3.189) is :

$$\cot\theta\, W_z\left\{(A_N^*)_x \cos\chi - (A_N^*)_y \sin\chi\right\}$$

$$= \cot\theta\;\cos\chi\, p_\chi\,(A_N^*)_x - \sin\chi\, p_\chi\,(A_N^*)_y$$

$$+ \cot\theta\left[W_z, (A_N^*)_x \cos\chi - (A_N^*) \sin\chi\right] \qquad (3.190)$$

$$- \cot\theta\left[\cos\chi\; p_\chi, (A_N^*)_x\right] + \cot\theta\left[\sin\chi\; p_\chi, (A_N^*)_y\right]$$

Now taking the full form for $\underline{A}_N^*$ , we obtain :

$$(A_N^*)_x = F \sum_\alpha Z_\alpha r_{\alpha z}^o ( H_x R_{\alpha z} - H_z R_{\alpha x} ) \qquad (3.191)$$

$$(A_N^*)_y = F \sum_\alpha Z_\alpha r_{\alpha z}^o ( H_y R_{\alpha z} - H_z R_{\alpha y} ) \qquad (3.192)$$

where $F = - \frac{eI''}{2cI}$ , and all components of vectors refer to the new set of axes (after rotation by $\chi$ ).

$$\left[ W_z, (A_N^*)_x \right] = - i\hbar F \sum_\alpha Z_\alpha r_{\alpha z}^o H_z ( r_{\alpha y} - 2r_{iy} ) \qquad (3.193)$$

$$\left[ W_z, (A_N^*)_y \right] = i\hbar F \sum_\alpha Z_\alpha r_{\alpha z}^o H_z ( r_{\alpha x} - 2r_{iy} ) \qquad (3.194)$$

Now $\underline{H}$ and $\underline{R}$, being space-fixed quantities, have implied $\chi$ dependence so that :

$$\begin{aligned} \left[ p_\chi, (A_N^*)_x \right] &= - i\hbar F \sum_\alpha Z_\alpha r_{\alpha z}^o ( H_y R_{\alpha z} - H_z R_y ) \\ &= - i\hbar (A_N^*)_y - \left[ W_z, (A_N^*)_y \right] \qquad (3.195) \end{aligned}$$

$$\begin{aligned} \left[ p_\chi, (A_N^*)_y \right] &= - i\hbar F \sum_\alpha Z_\alpha r_{\alpha z}^o ( -H_x R_{\alpha z} + H_z R_x ) \\ &= i\hbar F (A_N^*)_x - \left[ W_z, (A_N^*)_x \right] \qquad (3.196) \end{aligned}$$

Hence (3.190) becomes :

$$\begin{aligned} \cot\theta \, W_z \left\{ (A_N^*)_x \cos\chi - (A_N^*)_y \sin\chi \right\} &= i\hbar \cot\theta \left\{ (A_N^*)_x \sin\chi - (A_N^*)_y \cos \right. \\ &+ \cot\theta \cos\chi \, p_\chi \, (A_N^*)_x - \cot\theta \sin\chi \, p_\chi \, (A_N^*)_y \end{aligned}$$

(3.197)

Therefore :

$$\mathcal{H}_{RZ} = B\ (\underline{J} - \underline{W}) \cdot \underline{A}_N^* + \underline{A}_N^* \cdot (\underline{J} - \underline{W}) \qquad (3.198)$$

The susceptibility term $A_N^2$ remains essentially unchanged; it is a scalar product, independent of momenta, and is left unaffected on rotation. The same is true of all the remaining terms in (3.178) since all these remaining momenta commute with $\chi$.

To all these terms should be added those representing magnetic and other small interactions between particles; these are essentially the same as those for a general molecule, given in (3.94). After the unitary transformation :

$$\mathcal{H}'' = B^{-\frac{1}{2}} \Big[ \sum_i \Big\{ \underline{B}_i \cdot \underline{\Pi}_i + C\,\pi_i^4 + \sum_j \underline{\Pi}_i \cdot \underline{\underline{D}}_{ij} \cdot \underline{\Pi}_j + \sum_\alpha \underline{\Pi}_i \cdot \underline{\underline{D}}_{i\alpha} \cdot \underline{\Pi}_\alpha \Big\} + \sum_\alpha \underline{B}_\alpha \cdot \underline{\Pi}_\alpha \Big] B^{\frac{1}{2}} \qquad (3.199)$$

where we have taken into account the renormalization of the wave-function by pre-multiplying by $B^{-\frac{1}{2}}$ and post-multiplying by $B^{\frac{1}{2}}$. Also the space-fixed momenta are replaced by the slightly modified functions of molecular momenta :

$$\underline{\Pi}_i = \underline{\pi}_i + \frac{m}{M}\underline{\Pi} \qquad (3.200)$$

$$\underline{\Pi}_\alpha = \frac{m_\alpha}{M}\underline{\Pi} - \frac{m_\alpha}{M_N}\pi_i + \sum_r \sqrt{m_\alpha}\,\underline{\ell}_{\alpha r}\Pi_r - m_\alpha\, I''^{-1}\underline{r}^0_\alpha \wedge \underline{\Omega} \qquad (3.201)$$

## 3.7 Simplification of the Hamiltonian for a Linear Molecule

In this section it is proposed that the Hamiltonian will be simplified in a similar manner to that for the general molecule given in section 3.5 . As before, those terms which give a negligible contribution in a product representation of the wave-function will be neglected. With this in mind, we take the expressions (3.179) to (3.182) for the vector potentials.

The translational Hamiltonian is exactly the same as before :

$$\mathcal{H}_T = \frac{1}{2M} ( \underline{P} + \underline{A} )^2 \tag{3.202}$$

This term is usually neglected.

The rotational Hamiltonian (in its isomorphic form) is given by :

$$\mathcal{H}_R = B ( \underline{N} + \underline{A}_N )^2 \tag{3.203}$$

This has the same form as for a spherical-top molecule, but it should be remembered that the z-components of both $\underline{N}$ and $\underline{A}_N$ are identically zero. Expanding (3.203) gives respectively, the normal rotational kinetic energy, the rotational Zeeman effect and the rotational contribution to the molecular diamagnetism.

The vibrational Hamiltonian can be significantly simplified .

$$\sum_r B^{\frac{1}{2}} P_r B^{-1} P_r B^{\frac{1}{2}} = \sum_r P_r^2 + \sum_r B^{\frac{1}{2}} (P_r^2 B^{-\frac{1}{2}})$$

$$= \sum_r P_r^2 \qquad (3.204)$$

since $B^{-\frac{1}{2}}$ is only first order in $Q_r$. Also $P_r$ commutes with $A_r$ so that :

$$\sum_r \left\{ A_r B^{-\frac{1}{2}} P_r B^{\frac{1}{2}} + B^{\frac{1}{2}} P_r B^{-\frac{1}{2}} A_r \right\} = \sum_r 2 A_r P_r \qquad (3.205)$$

Collecting all these terms together :

$$\mathcal{H}_V = \sum_r \tfrac{1}{2} ( P_r^2 + 2 A_r P_r + A_r^2 ) \qquad (3.206)$$

These are respectively, the vibrational kinetic energy, the vibrational Zeeman term and the vibrational contribution to the molecular diamagnetism. The vibrational Zeeman term can be re-written as :

$$\mathcal{H}_{VZ} = - \sum_{\alpha, r} \frac{Z_\alpha e}{2c} \underline{H} \cdot \underline{r}_\alpha \wedge \frac{\underline{\ell}_{\alpha r}}{\sqrt{m}} P_r \qquad (3.207)$$

This only gives non-zero diagonal contributions if r belongs to a degenerate (i.e. bending) mode of vibration. Then if second order effects can be neglected and $Z_\alpha / m_\alpha$ can be replaced by $Z_{eff}/M$, the above approximates to :

$$\mathcal{H}_{VZ} = - \frac{Z_{eff} e}{2Mc} \underline{H} \cdot \underline{G} \qquad (3.208)$$

the form one might intuitively have expected.

The electronic Hamiltonian is unchanged for a linear molecule :

$$\begin{aligned}\mathcal{H}_e = {} & \sum_i \frac{1}{2m} p_i^2 + \frac{1}{2M_N}\Big(\sum_i \underline{p}_i\Big)^2 - \frac{1}{8m^3c^2}\sum_i p_i^4 \\ & + \frac{e}{2mc}\sum_i \underline{H}\cdot\Big[\underline{r}_i\big(1-\frac{m}{M}\big) - \frac{m}{M}\sum_{j\neq i}\underline{r}_j\Big]\wedge\underline{p}_i \qquad (3.209) \\ & - \frac{e}{4m^3c^3}\sum_i \underline{H}\cdot(\underline{r}_i\wedge\underline{p}_i)p_i^2 + \frac{e^2}{2mc^2}\sum_i A_i^2\end{aligned}$$

The remaining terms follow the same form as those for the general molecule.

$$\begin{aligned}\mathcal{H}_1 = {} & \sum_i\Bigg[\sum_{j\neq i}\frac{g\beta e}{2mc}\,\frac{1}{r_{ij}^3}\,\underline{s}_i\cdot(2\underline{r}_{ij}\wedge\underline{p}_j - \underline{r}_{ij}\wedge\underline{p}_i) \\ & + \sum_\alpha\Bigg\{\frac{g\beta e}{2mc}\,\frac{Z_\alpha}{r_{i\alpha}^3}\,\underline{s}_i\cdot(\underline{r}_{i\alpha}\wedge\underline{p}_i) + \frac{g_\alpha\beta_N e}{mc}\,\frac{1}{r_{i\alpha}^3}\,\underline{I}_\alpha\cdot(\underline{r}_{i\alpha}\wedge\underline{p}_i)\Bigg\}\Bigg] \\ & + \sum_i\frac{g}{2mc}\,\underline{s}_i\cdot(\underline{E}\wedge\underline{p}_i) \qquad (3.210)\end{aligned}$$

These are, respectively, the spin-orbit interactions, the nuclear spin orbit hyperfine interaction and the interaction of the magnetic moment of a moving electron with a static electric field.

$$\mathcal{H}_2 = \sum_{\alpha,i,j}\frac{Z_\alpha g\beta e}{M_N c}\,\frac{1}{r_{i\alpha}^3}\,\underline{s}_i\cdot(r_{i\alpha}\wedge\underline{p}_j)$$

$$- \sum_{\alpha,i,r} \frac{Z_\alpha g\beta e}{m\ c} \frac{1}{r_{i\alpha}^3} B^{\frac{1}{2}} \underline{s}_i \cdot (\underline{r}_{i\alpha} \wedge \underline{\ell}_{\alpha r})\ P_r\ B^{-\frac{1}{2}}$$

$$+ \sum_{\alpha,i} \frac{Z_\alpha g\beta e}{c} \frac{1}{r_{i\alpha}^3} B^{\frac{1}{2}} \underline{s}_i \cdot I''^{-1} \underline{r}_{i\alpha} \wedge (\underline{r}_\alpha^o \wedge \underline{N})\ B^{-\frac{1}{2}} \qquad (3.211)$$

These are the mass-polarization correction to the spin-orbit coupling, the spin-vibration interaction which manifests itself in degenerate vibrational states with a form $\underline{s}_i \cdot \underline{G}$, and the spin-rotation interaction, which differs slightly from the expression for the general molecule.

$$\mathcal{H}_3 = \sum_i \sum_{i \neq j} - \frac{e^2}{4m^2c^2} \underline{p}_i \cdot \left(\frac{1}{r_{ij}} + \underline{r}_{ij} \frac{1}{r_{ij}^3} \underline{r}_{ij}\right) \cdot \underline{p}_j$$

$$- \sum_i \frac{g\beta}{2m^2c^2} (\underline{s}_i \cdot \underline{H}) p_i^2 \qquad (3.212)$$

These terms are respectively the orbit-orbit interaction and the relativistic correction to the electron-spin Zeeman interaction. These are identical to the corresponding terms for a non-linear molecule.

$$\mathcal{H}_4 = \sum_{\alpha,i,j} - \frac{Z_\alpha e^2}{2mM_N c^2} \underline{p}_i \cdot \left(\frac{1}{r_{i\alpha}} + \underline{r}_{i\alpha} \frac{1}{r_{i\alpha}^3} \underline{r}_{i\alpha}\right) \cdot \underline{p}_j$$

$$+ \sum_{\alpha,i} \frac{Z_\alpha e^2}{2m\sqrt{m_\alpha}\,c^2} B^{\frac{1}{2}} \underline{p}_i \cdot \left(\frac{1}{r_{i\alpha}} + \underline{r}_{i\alpha} \frac{1}{r_{i\alpha}^3} \underline{r}_{i\alpha}\right) \cdot \left(\sum_r \underline{\ell}_{\alpha r} P_r\right) B^{-\frac{1}{2}}$$

$$- \sum_{\alpha, i} \frac{Z_\alpha e^2}{2mc^2} \underline{p}_i \cdot \left( \frac{1}{r_{i\alpha}} + \underline{r}_{i\alpha} \frac{1}{r_{i\alpha}^3} \underline{r}_{i\alpha} \right) \cdot \left( \underline{r}^c_{\alpha} \wedge \underline{N} \right) I''^{-1} \qquad (3.213)$$

These give the mass-polarization correction to the orbit-orbit interaction, the orbit-vibration and the orbit-rotation interaction. To these should be added the potential energy term, V.

$$\begin{aligned} V = \sum_i \Big[ & mc^2 - e\phi_i + g\, \underline{s}_i \cdot \underline{H} + \sum_{j \neq i} \Big\{ \frac{e^2}{2r_{ij}} - \frac{e^2 \hbar^2}{2m^2 c^2} \delta(r_{ij}) \\ & + \tfrac{1}{2} g^2 \beta^2 \frac{1}{r_{ij}^3} \underline{s}_i \cdot \underline{s}_j - \frac{3}{r_{ij}^5} (\underline{s}_i \cdot \underline{r}_{ij})(\underline{s}_j \cdot \underline{r}_{ij}) - \frac{8\pi}{3} \delta(r_{ij})\, \underline{s}_i \cdot \underline{s}_j \Big\} \\ & + \sum_\alpha \Big\{ - \frac{Z_\alpha e^2}{r_{i\alpha}} + \frac{Z_\alpha e^2 \hbar^2}{2m^2 c^2} \delta(r_{i\alpha}) \\ & - g g_\alpha \beta \beta_N \frac{1}{r_{i\alpha}^3} \underline{s}_i \cdot \underline{I}_\alpha - \frac{3}{r_{i\alpha}^5} (\underline{s}_i \cdot \underline{r}_{i\alpha})(\underline{I}_\alpha \cdot \underline{r}_{i\alpha}) - \frac{8\pi}{3} \delta(r_{i\alpha})\, \underline{s}_i \cdot \underline{I}_\alpha \Big\} \Big] \\ & + \sum_\alpha \Big\{ m_\alpha c^2 + Z_\alpha e \phi_\alpha - g_\alpha \beta_N \underline{I}_\alpha \cdot \underline{H} + \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{2r_{\alpha\beta}} \Big\} + \mathcal{H}_Q \end{aligned} \qquad (3.214)$$

These terms have been discussed in section 3.2; they are the same except that the space-fixed coordinates $R_{\lambda\mu}$ have been replaced by their corresponding distances $r_{\lambda\mu}$ in the molecule-fixed axis system

The above Hamiltonian, given in (3.202) to (3.214), is appropriate to any linear molecule but in certain special cases can be substantially simplified.

For example, in the diatomic molecule, the vibrational angular momentum goes to zero and the intermediate moment of inertia becomes :

$$I'' = \sum_{\alpha} m_{\alpha} r_{\alpha}^2 = \frac{m_1 m_2}{(m_1 + m_2)} r^2 \qquad (3.215)$$

where r is the internuclear distance.

Making these modifications gives a total Hamiltonian that is in agreemant with that by other authors (e.g. ref. 33) except that here all the mass-polarization corrections have been included.

If we have a spin wave-function quantised in the molecular frame, it automatically has implicit Euler angle dependence and thus can be operated on by the rotational operators, $\underline{J}$. Ideally, one would like $\underline{J}$ to act only on the rotational wave-functions and this can be done if $\underline{J}$ is replaced by $\underline{J}-\underline{S}$ everywhere it appears in the Hamiltonian; $\underline{S}$ is the total electron spin operator (see Appendix B). The rotational Hamiltonian is thus obtained by replacing $\underline{N}$ by $\underline{J}-\underline{G}-\underline{L}-\underline{S}$ instead of $\underline{J}-\underline{G}-\underline{L}$.

# Appendix A

## Transformation of Tensor Quantities in Curvilinear Coordinates

Let us consider a $\nu$-dimensional Cartesian space, $x^{\mu}$ which transforms into the curvilinear coordinates $q^{i}$. They are contravariant vectors since they transform like :

$$\bar{A}^{m} = \frac{\partial \bar{x}^{m}}{\partial x^{i}} A^{i} \qquad \text{(repeated suffix convention)} \tag{A.1}$$

where the bar implies a new coordinate system. Similarly covariant components (with suffices instead of superfixes) are defined according to :

$$\bar{B}_{m} = \frac{\partial x^{i}}{\partial \bar{x}^{m}} B_{i} \tag{A.2}$$

The distance between two points in the curvilinear coordinate system is given by :

$$ds^{2} = g_{ij}\, dq^{i}\, dq^{j} \tag{A.3}$$

where,

$$g_{ij} = \frac{\partial x^{\mu}}{\partial q^{i}} \frac{\partial x^{\mu}}{\partial q^{j}} = g_{ji} \tag{A.4}$$

The Jacobian for the transformation (which relates the volume elements in the two axis systems) is given by :

$$J = \left| \frac{\partial x^{\mu}}{\partial q^{i}} \right| \tag{A.5}$$

$$J^2 = \left| \frac{\partial x^{\mu}}{\partial q^{i}} \frac{\partial x^{\mu}}{\partial q^{j}} \right|$$

$$= \left| g_{ij} \right| = g \quad \text{say} \tag{A.6}$$

The volume element in the $\nu$-dimensional phase space is :

$$d\tau = \cdots dx\, dx \cdots = \sqrt{g} \cdots dq^{i} dq^{j} \cdots \tag{A.7}$$

Any infinitesimal change in the position vector in phase space is :

$$d\underline{r} = \frac{\partial \underline{r}}{\partial q^{i}} dq^{i} = \underline{e}_{i}\, dq^{i} \tag{A.8}$$

where $\underline{e}_i$ is a basis vector in the new space (but not normalised) If no two $\underline{e}_i$ are parallel, it is possible to define a reciprocal set of vectors $\underline{e}^j$ such that :

$$\underline{e}_{i} \cdot \underline{e}^{j} = \delta_{ij} \tag{A.9}$$

and $$d\underline{r} = \underline{e}^{j}\, dq_{j} \tag{A.10}$$

For any general vector, $\underline{A}$

$$\underline{A} = a^{i}\, \underline{e}_{i} = a_{j}\, \underline{e}^{j} \tag{A.11}$$

where $a^i$ and $a_j$ are respectively the contravariant and covariant components of $\underline{A}$ . The distance element in (A.3) can be re-written

$$ds^2 = d\underline{r}.d\underline{r} = \underline{e}_i . \underline{e}_j \, dq^i \, dq^j \tag{A.12}$$

$$= \underline{e}^i . \underline{e}^j \, dq_i \, dq_j \tag{A.13}$$

Therefore,

$$g_{ij} = \underline{e}_i . \underline{e}_j \tag{A.14}$$

and also the inverse matrix,

$$g^{ij} = \underline{e}^i . \underline{e}^j \tag{A.15}$$

Post-multiplying (A.14) by $\underline{e}^j$ and summing over j gives

$$\underline{e}_i = g_{ij} \, \underline{e}^j \; ; \text{ also } \; \underline{e}^i = g^{ij} \, \underline{e}_j \tag{A.16}$$

In terms of these, the gradient of a scalar will transform as :

$$\underline{\nabla}\phi = \frac{\partial q^i}{\partial x^\mu} \frac{\partial \phi}{\partial q^i} = \underline{e}^i \frac{\partial \phi}{\partial q^i}$$

$$= g^{ij} \, \underline{e}_j \frac{\partial \phi}{\partial q^i} \tag{A.17}$$

The divergence of a vector V will be taken to be the covariant derivative. Thus :

$$\underline{\nabla}.\underline{V} = \frac{\partial V^\mu}{\partial x^\mu} = \frac{\partial q^i}{\partial x^\mu} \frac{\partial}{\partial q^i} \left\{ V^j \frac{\partial x^\mu}{\partial q^j} \right\} \tag{A.18}$$

$$= \delta_{ij} \frac{\partial V^j}{\partial q^i} + V^j \frac{g^{ik}}{2} \frac{\partial g_{ik}}{\partial q^j}$$

$$= \frac{1}{2g} \frac{\partial g}{\partial g_{ik}} \frac{\partial g_{ik}}{\partial q^j} = \frac{\partial V^i}{\partial q^i} + \frac{V^j}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^j}$$

Therefore,
$$\underline{\nabla} . \underline{V} = \frac{1}{\sqrt{g}} \frac{\partial(\sqrt{g}\, V^i)}{\partial q^i} \tag{A.19}$$

If,
$$\underline{V} = \nabla\phi \quad ; \quad V^i = g^{ij} \frac{\partial\phi}{\partial q^j} \tag{A.20}$$

Then,
$$\nabla^2\phi = \underline{\nabla}.(\nabla\phi)$$
$$= \frac{1}{\sqrt{g}} \frac{\partial}{\partial q_i} \left\{ \sqrt{g}\, g^{ij} \frac{\partial\phi}{\partial q^j} \right\} \tag{A.21}$$

## Appendix B

## Effect of Rotation Operators on Case (a) Spin Wave-functions

The molecule fixed (case a) wave-function $|S\Sigma\rangle$ has implicit Euler angle dependence and thus can be operated on by the rotation operators. For a single electron spin ($s=\frac{1}{2}$), we can write the Euler angle dependence as

$$\psi(s\sigma) = \sum_{m} \mathcal{D}^{\frac{1}{2}}_{m\sigma}(\omega)\ \psi(sm) \qquad (B.1)$$

where $\omega$ signifies the three Euler angles $(\alpha,\beta,\gamma)$ and $\mathcal{D}^{\frac{1}{2}}_{m\sigma}(\omega)$ is a rotation matrix, to be defined in the next chapter, but can be written explicitly as a 2x2 matrix as below.

$$\mathcal{D}^{\frac{1}{2}}_{m\sigma}(\omega) = \begin{pmatrix} \exp -i(\alpha+\gamma)/2 \cos \beta/2 & -\exp i(\alpha-\gamma)/2 \sin \beta/2 \\ \exp i(\gamma-\alpha)/2 \sin \beta/2 & \exp i(\alpha+\gamma)/2 \cos \beta/2 \end{pmatrix} \qquad (B.2)$$

where $m=\pm\frac{1}{2}$ labels the columns and $\sigma=\pm\frac{1}{2}$ labels the rows. N.B. We shall from now on use the symbols $(\alpha,\beta,\gamma)$ instead of $(\phi,\theta,\chi)$ to express the orientation of the molecular axis system.

The differential operators appearing in the rotational operator $\underline{J}$ will be written as $(\frac{\partial}{\partial\beta})_s$ etc. to signify that it operates on the complete Euler angle dependence of the wave-function, and as $(\frac{\partial}{\partial\beta})_m$ etc. when the electron spins are molecule-quantised and only the rotational wave-function is operated on. Now consider a wave-function that is the product of a rotational wave-function and a single electron spin wave-function, $R(\alpha,\beta,\gamma)\,\psi(\sigma)$.

Then,

$$\left(\frac{\partial}{\partial\gamma}\right)_s R(\alpha,\beta,\gamma)\,\psi(\sigma) = \left(\frac{\partial}{\partial\gamma}\right)_m R(\alpha,\beta,\gamma)\,\psi(\sigma) + R(\alpha,\beta,\gamma)\left(\frac{\partial}{\partial\gamma}\right)_s \psi(\sigma) \tag{B.3}$$

But,

$$\begin{aligned}\left(\frac{\partial}{\partial\gamma}\right)_s \psi(\sigma) &= \sum_m \left(\frac{\partial}{\partial\gamma}\right)_s \mathfrak{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,\psi(m)\\ &= i/2\ (-1)^{\frac{1}{2}+\sigma}\,\psi(\sigma)\\ &= -i\ s_z\ \psi(\sigma)\end{aligned} \tag{B.4}$$

where $s_z$ is the molecular z-component of the electron-spin operator in dimensionless units ($\hbar=1$). Similarly,

$$\begin{aligned}\left(\frac{\partial}{\partial\beta}\right)_s \psi(\sigma) &= \sum_m \left(\frac{\partial}{\partial\beta}\right)_s \mathfrak{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,\psi(m)\\ &= \tfrac{1}{2}\ (-1)^{\frac{1}{2}-\sigma}\ \psi(-\sigma)\ \exp -2i\sigma\gamma\ \text{(using B.2)}\\ &= \tfrac{1}{2}\,\psi(-\sigma)\ (-1)^{\frac{1}{2}-\sigma}\left[\cos\gamma + i(-1)^{\frac{1}{2}+\sigma}\sin\gamma\right]\end{aligned} \tag{B.5}$$

Now

$$s_x\,\psi(\sigma) = \tfrac{1}{2}(s_+ + s_-)\,\psi(\sigma) = \tfrac{1}{2}\psi(-\sigma) \tag{B.6}$$

and

$$is_y\,\psi(o) = \tfrac{1}{2}(s_+ - s_-)\,\psi(\sigma) = \tfrac{1}{2}(-1)^{\frac{1}{2}+\sigma}\psi(-\sigma) \tag{B.7}$$

Therefore :

$$\left(\frac{\partial}{\partial\beta}\right)_s \psi(\sigma) = -i(s_x\ \sin\gamma + s_y\ \cos\gamma)\,\psi(\sigma) \tag{B.8}$$

$$\left(\frac{\partial}{\partial\beta}\right)_s = \left(\frac{\partial}{\partial\beta}\right)_m - i(s_x \sin\gamma + s_y \cos\gamma) \qquad (B.10)$$

$$\left(\frac{\partial}{\partial\alpha}\right)_s \psi(\sigma) = \sum_m \left(\frac{\partial}{\partial\alpha}\right)_s \mathscr{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,\psi(m)$$

$$= \sum_m \tfrac{1}{2}(-1)^{\frac{1}{2}+m}\,\mathscr{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,\psi(m)$$

But, since $1 = 2\cos^2\beta/2 - \cos\beta = 2\sin^2\beta/2 + \cos\beta$

$$\left(\frac{\partial}{\partial\alpha}\right)_s \psi(\sigma) = i/2\,(-1)^{\frac{1}{2}+m}\Big\{\psi(m)\,\mathscr{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,(2\sin^2\beta/2 + \cos\beta)$$
$$+\,\psi(-m)\,\mathscr{D}^{\frac{1}{2}}_{-m\sigma}(\omega)\,(2\cos^2\beta/2 - \cos\beta)\Big\}$$
with $m=\sigma$

$$= i/2 \sum_m (-1)^{\frac{1}{2}+\sigma}\,\mathscr{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,\psi(m)\,\cos\beta$$
$$+\; i/2 \sum_m \mathscr{D}^{\frac{1}{2}}_{m\sigma}(\omega)\,\psi(m)\,\sin\beta\,\exp -2i\sigma\gamma$$

$$= i/2\,(-1)^{\frac{1}{2}+\sigma}\cos\beta\;\psi(\sigma)$$
$$+\; i\sin\beta\Big\{\cos\gamma + i(-1)^{\frac{1}{2}+\sigma}\sin\gamma\Big\}\,\psi(-\sigma)$$

$$= \Big\{-is_z\cos\beta + i\,\sin\beta\,(s_x\cos\gamma - s_y\sin\gamma)\Big\}\,\psi(\sigma) \qquad (B.11)$$

Now if the spin-wave-function of each electron, in turn, is operated on by $\frac{\partial}{\partial\alpha}$, $\frac{\partial}{\partial\beta}$, and $\frac{\partial}{\partial\gamma}$, then the components of spin of one electron must be replaced by the sum of the components of the individual electrons. Thus if $\underline{S}$ is the total spin operator (in units of $\hbar=1$),

$$\left(\frac{\partial}{\partial\alpha}\right)_s = \left(\frac{\partial}{\partial\alpha}\right)_m + i\sin\beta\,(S_x\cos\gamma - S_y\sin\gamma) - iS_z\cos\beta \tag{B.12}$$

$$\left(\frac{\partial}{\partial\beta}\right)_s = \left(\frac{\partial}{\partial\beta}\right)_m - i\,(S_x\sin\gamma + S_y\cos\gamma) \tag{B.13}$$

$$\left(\frac{\partial}{\partial\gamma}\right)_s = \left(\frac{\partial}{\partial\gamma}\right)_m - i\,S_z \tag{B.14}$$

These can now be substituted into the expressions for the rotational angular momentum, (3.79) to (3.83). Thus

$$J_x \longrightarrow J_x - S_x \tag{B.15}$$

$$J_y \longrightarrow J_y - S_y \tag{B.16}$$

$$J_z \longrightarrow J_z - S_z \tag{B.17}$$

where the rotational operators on the right hand side of the above expressions act only on the explicit rotational dependence of the wave-function, i.e. only on the rotational wave-function.

## References to Chapter 3

1. J. Gerratt, Ann. Rep. Prog. Chem. (Chem. Soc. London) A65, 3 (1968).
2. R. F. Curl, Mol. Phys. 9, 585 (1965).
3. P. A. M. Dirac, "The Principles of Quantum Mechanics", (Oxford University Press, London, 1958).
4. M. E. Rose, "Relativistic Electron Theory", (John Wiley and Sons Inc., New York, 1961).
5. A. Messiah, "Quantum Mechanics", vol II, (North-Holland Publishing Co., Amsterdam, 1965).
6. L. L. Foldy and S. A. Wouthuysen, Phys. Rev. 78, 29 (1950).
7. G. Breit, Phys. Rev. 34, 553 (1929).
8. Z. V. Chraplyvy, Phys. Rev. 91, 388 (1953), ibid. 92, 1310 (1953).
9. W. A. Barker and F. N. Glover, Phys. Rev. 99, 317 (1955).
10. L. H. Thomas, Nature 117, 514 (1926).
11. A. Abragam and J. H. Van Vleck, Phys. Rev. 92, 1448 (1953).
12. P. W. Atkins and A. M. Jamieson, Mol. Phys. 14, 425 (1967).
13. C. G. Darwin, Phil. Mag. 39, 537 (1920).
14. T. Itoh, Rev. Mod. Phys. 37, 159 (1965).
15. H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-electron Atoms", (Springer-Verlag, Berlin, 1957).
16. R. A. Hegstrom, Phys. Rev. 184, 17 (1969).
17. E. B. Wilson and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

18. B. T. Darling and D. M. Dennison, Phys. Rev. 57, 128 (1940).

19. E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", (McGraw-Hill, New York, 1955).

20. C. Eckart, Phys. Rev. 47, 552 (1935).

21. H. Marganau and G. M. Murphy, "The Mathematics of Physics and Chemistry", Chap. 4, (Van Nostrand, Princeton, 1956).

22. B. Podolsky, Phys. Rev. 32, 812 (1928).

23. E. C. Kemble, "The Fundamental Principles of Quantum Mechanics", Sec. 35b, (McGraw-Hill, New York, 1937).

24. C. P. Slichter, "Principles of Magnetic Resonance", Sec. 4.4, (Harper and Row, New York, 1963).

25. D. W. Davies, "The Theory of the Electric and Magnetic Properties of Molecules", Sec 2.3, (John Wiley, London, 1967).

26. J. K. G. Watson, Mol. Phys. 15, 479 (1968).

27. J. H. Van Vleck, Phys. Rev. 33, 467 (1929)

28. H. H. Nielsen, Rev. Mod. Phys. 23, 90 (1951).

29. G. Amat and L. Henry, Cah. Phys. 12, 273 (1958).

30. J. K. G. Watson, Mol. Phys. (to be published).

31. J. T. Hougan, J. Chem. Phys. 36, 319 (1962).

32. D. M. Brink and G. R. Satchler, "Angular Momentum", (Oxford University Press, London, 1968).

33. A. Carrington, D. H. Levy and T. A. Miller, Adv. Chem. Phys. (to be published).

# Chapter 4

# ANGULAR MOMENTUM THEORY

## 4.1 Introduction

The concept of rotational invariance plays an important part in the analysis of physical systems; for example in the absence of external fields and considering a molecule to be an indepedent entity, its Hamiltonian remains unchanged after a rotation, i.e. the Hamiltonian commutes with the infinitesimal rotation operator. This leads to the concept of angular momentum and irreducible spherical tensor operators, in terms of which the Hamiltonian can be written. The use of these techniques simplifies the evaluation of matrix elements and the basic principles involved are given below. Also we attempt to clear up some misconceptions of other authors. Finally important matrix elements are evaluated.

## 4.2 Rotation Operators

A rotation can be considered in either an active or a passive sense. In an example where we are transforming from one axis system to another, it might seem preferable to have an operator which rotates the axis system from one position to the second. This is essentially the passive operator of Edmonds [1] and others [2-4]. Although this is easy to define, it is found rather difficult to use.

Instead we shall follow the method of Brink and Satchler [5] and other authors [6,7] who define their rotation operators as those which rotate the physical system from one position to another. For the two-dimensional case, consider a function $\psi$ which depends upon the polar coordinate $\phi$. Then rotation of the system by an angle $\alpha$, transforms the wavefunction in such a way that the new wavefunction at point $\phi + \alpha$ is equal to the old function at $\phi$.

$$\therefore \quad \psi'(\phi) = R(\alpha)\psi(\phi) = \psi(\phi - \alpha) \qquad (4.1)$$

or for small rotations :

$$\begin{aligned} \lim_{\alpha \to 0} R(\alpha) &= 1 - \alpha\frac{\partial}{\partial\phi} \\ &= 1 - i\alpha\frac{L_\phi}{\hbar} \end{aligned} \qquad (4.2)$$

where $L_\phi$ is the angular momentum operator. For any general rotation of the system through a small angle $\alpha$ about an axis $\underline{n}$ :

$$R_n(\alpha) = 1 - i\alpha\underline{J}.\underline{n} \qquad (4.3)$$

where $\underline{J}$ is the total angular momentum operator (in units of $\hbar$). A finite rotation is a succession of infinitesimal rotations so that :

$$R_n(\alpha) = \exp\left[-i(\underline{J}.\underline{n})\alpha\right] \qquad (4.4)$$

Since two rotations do not in general commute, it is found that :

$$J_x J_y = J_y J_x + iJ_z$$

or the commutator, $\left[J_x, J_y\right] = iJ_z$ and cyclic order (4.5)

These commutation relations are the definitions of true angular momentum operators.

## 4.3 Irreducible Representations of the Rotation Group

Consider a finite manifold that is an irreducible representation $\Delta$ of the rotation group. Any finite rotation can be produced by a succession of infinitesimal rotations, so that a necessary and sufficient condition that $\Delta$ is irreducible is that it is irreducible to the operators $J_x$, $J_y$, and $J_z$.

Now let the ket $|jm\rangle$ be an eigenvector of $J_z$ with eigenvalue m, which has a maximum value of j. Then

$$J_z |jm\rangle = m|jm\rangle \tag{4.6}$$

The operators defined by : $J_\pm = J_x \pm iJ_y$ have the commutation relations :

$$\left[J_\pm , J_z\right] = \mp J_\pm \tag{4.7}$$

and are found to be the raising and lowering operators, changing m by ±1.

$$J_\pm |jm\rangle = \left[j(j+1) - m(m\pm1)\right]^{\frac{1}{2}} |j,m\pm1\rangle \tag{4.8}$$

Here the arbitrary phase factor is chosen according to the convention of Condon and Shortley.[8] This representation, $\mathcal{D}_j$, has a degeneracy of $2j+1$ ($m = j, j-1, j-2, \cdots\cdots, -j$). Also $2j$ must be an integer; therefore half-integral $j$ is allowed.

For integral $j$ ($=l$), the eigenfunctions are the spherical harmonics.

$$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\, e^{im\phi} \qquad (4.9)$$

where

$$\Theta_{lm}(\theta) = (-1)^m \frac{(2l+1)(l-m)!}{2(l+m)!} P_l^m(\theta), \quad \text{if } m \geqslant 0$$

$$= (-1)^m \Theta_{l|m|}(\theta), \quad \text{if } m < 0 \qquad (4.10)$$

and $P_l^m(\theta)$ is the associated Legendre polynomial[9].

## 4.4 Rotation Matrices

Using the rotation operators defined in section 4.2, it is possible to specify the effect of any general rotation. If a set of orthogonal axes $(x,y,z)$ are rotated to new positions $(x',y',z')$, their relative orientation can be specified by the Euler angles $(\alpha,\beta,\gamma)$ which are defined by the following right-hand screw rotations.

First the axes are rotated about the z axis by an angle $\alpha$ to new positions $(x_1,y_1,z)$. Then they are rotated by $\beta$ around the $y_1$ axis to give $(x_2,y_1,z')$, and finally through an angle $\gamma$ about the z' axis.

If the system is rotated by $(\alpha,\beta,\gamma)$, the rotation operator corresponding to this rotation (cf. section 4.2) is:

$$D(\alpha,\beta,\gamma) = \exp(-i\gamma J_{z'})\exp(-i\beta J_{y_1})\exp(-i\alpha J_z) \qquad (4.11)$$

Alternatively this rotation can be obtained in terms of rotations about the original axes. Then :

$$D(\alpha,\beta,\gamma) = \exp(-i\alpha J_z)\exp(-i\beta J_y)\exp(-i\gamma J_z) \qquad (4.12)$$

From here on we shall use $\omega$ as a short-hand for $(\alpha,\beta,\gamma)$.

In a manner similar to that in equation (4.1), the operation of $D(\omega)$ on a function $\Phi_{jm}(\theta,\phi)$, with angular dependence like a spherical harmonic, gives a new function of $\theta$ and $\phi$, equal to $\Phi_{jm}$ at $(\theta',\phi')$, the points rotated into $(\theta,\phi)$ by this operation.

$$\Phi'(\theta,\phi) = D(\omega)\,\Phi_{jm}(\theta,\phi) = \Phi_{jm}(\theta',\phi') \qquad (4.13)$$

and using the closure relationship :

$$\Phi'(\theta,\phi) = \sum_n \Phi_{jn}(\theta,\phi)\,\langle jn|D(\omega)|jm\rangle$$

$$= \sum_n \Phi_{jn}(\theta,\phi)\,\mathfrak{D}^j_{nm}(\omega) \qquad (4.14)$$

$\mathfrak{D}^j_{nm}(\omega)$ is the matrix representing the rotation $(\alpha,\beta,\gamma)$ in the

(2j+1) dimensional irreducible representation of the rotation group (corresponding to angular momentum j).

An alternative interpretation of (4.14), which will be much used later, is to consider $(\theta',\phi')$ as the coordinates of the old point $(\theta,\phi)$ measured in the new set of axes obtained by rotating the old axes with the system. Hence we have a relationship between spherical harmonic type functions in different axis systems at any general point in space.

Since $D(\omega)$ is an unitary operator :

$$\text{i.e.} \quad D^{\dagger}(\alpha,\beta,\gamma) = D(-\gamma,-\beta,-\alpha) \tag{4.15}$$

$$\begin{aligned} \langle jm|D^{-1}(\omega)|jm'\rangle &= \langle jm'|D(\omega)|jm\rangle^{*} \\ &= (\mathfrak{D}^{j}_{m'm})^{*} \end{aligned} \tag{4.16}$$

This yields :

$$\sum_{n} \mathfrak{D}^{j}_{m'n}(\omega)\left(\mathfrak{D}^{j}_{mn}(\omega)\right)^{*} = \delta_{m'm} \tag{4.17}$$

and

$$\sum_{n} \mathfrak{D}^{j}_{nm'}(\omega)\left(\mathfrak{D}^{j}_{nm}(\omega)\right)^{*} = \delta_{m'm} \tag{4.18}$$

Also it should be noted that :

$$\mathfrak{D}^{j}_{mn}(\omega) = \exp(-im\alpha - in\gamma)\, d^{j}_{mn}(\beta) \tag{4.19}$$

where

$$d^{j}_{mn}(\beta) = \langle jm|\exp(-i\beta J_y)|jn\rangle \tag{4.20}$$

The dependence of the rotation matrices on $\alpha$ and $\gamma$ suggests that they are also related to the symmetric top wavefunctions. If (4.14) and (4.13) are inverted and using (4.17) :

$$\Phi_{jn}(\theta,\phi) = \sum_m \left(\mathcal{D}^j_{nm}(\omega)\right)^* \Phi_{jm}(\theta',\phi') \qquad (4.21)$$

and chosing $\theta' = \phi' = 0$, so that $\phi = \alpha$, $\theta = \beta$ :

$$\Phi_{jn}(\beta,\alpha) = \sum_m \left(\mathcal{D}^j_{nm}(\alpha,\beta,\gamma)\right)^* \Phi_{jm}(0,0) \qquad (4.22)$$

Any further rotation $\gamma_o$ about z' changes each $\mathcal{D}^{j\,*}_{nm}$ by a phase factor, and provided all $\Phi_{jm}(0,0)$ except one are zero

$$\Phi_{jn}(\beta,\alpha) = k\left(\mathcal{D}^j_{nm}(\alpha,\beta,\gamma)\right)^* \qquad (4.23)$$

is an eigenfunction of $L_{z'}$. Hence $\left(\mathcal{D}^j_{nm}(\omega)\right)^*$ is proportional to the symmetric top wavefunction.

## 4.5 Coupling of Angular Momenta

In a system of two independent angular momenta $\underline{J}_1$ and $\underline{J}_2$, it is found that $\underline{J}_1^2$, $J_{1z}$, $\underline{J}_2^2$ and $J_{2z}$ are all commuting operators and that the corresponding eigenfunctions can be written as the product :

$$|\gamma j_1 j_2 m_1 m_2\rangle = \sum_{\gamma_1,\gamma_2} |\gamma_1 j_1 m_1\rangle\,|\gamma_2 j_2 m_2\rangle \qquad (4.24)$$

where the $\gamma$'s are all other quantum numbers necessary to specify the states. Alternatively, another set of commuting operators is $\underline{J}_1^2$, $\underline{J}_2^2$, $\underline{J}^2 = (\underline{J}_1 + \underline{J}_2)^2$ and $J_z = (J_{1z} + J_{2z})$ , with corresponding eigenfunctions $|\gamma j_1 j_2 JM\rangle$ . These are irreducible representations; however the product wave-functions are reducible representations of the complete rotation group.

The unitary transformation connecting these two representations is :

$$|j_1 j_2 JM\rangle = \sum_{m_1, m_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 JM\rangle \qquad (4.25)$$

and

$$|j_1 j_2 m_1 m_2\rangle = \sum_{J, M} |j_1 j_2 JM\rangle \langle j_1 j_2 JM | j_1 j_2 m_1 m_2\rangle \qquad (4.26)$$

where $\langle j_1 j_2 JM | j_1 j_2 m_1 m_2\rangle = \langle j_1 j_2 m_1 m_2 | j_1 j_2 JM\rangle$ are the vector-coupling or Clebsch-Gordon coefficients. They have non-zero values if all the j's can form a triangle (i.e. $j_1 + j_2 \geqslant J \geqslant |j_1 - j_2|$ ) and if $M = m_1 + m_2$ (since $J_z = J_{1z} + J_{2z}$). Their values are tabulated by many authors (see for example references 7 and 8).

The Clebsch Gordon coefficients are somewhat asymmetric to interchange of momenta and the more symmetrical Wigner 3-j symbols will be used here and in later chapters. They are defined by :

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} = (-1)^{j_1 - j_2 + M} (2J+1)^{-\frac{1}{2}} \langle j_1 j_2 m_1 m_2 | j_1 j_2 JM\rangle \qquad (4.27)$$

The values of certain 3-j symbolsare tabulated in Edmonds [1] and in Brink and Satchler [5] p.36 .

Any even permutation of columns of a 3-j symbol leaves its numerical value unchanged, while an odd permutation is equivalent to multiplication by $(-1)^{j_1+j_2+J}$. Thus the order of vector-coupling can change the result by a phase factor.

When three angular momenta are coupled together, the result is no longer unique even to a phase factor; it depends upon the order of coupling of the original momenta. For example, $\underline{j}_1$ and $\underline{j}_2$ can be coupled to give $\underline{j}_{12}$ and this with $\underline{j}_3$ to give the resultant $\underline{J}$. Alternatively the resultant $\underline{j}_{23}$ from adding $\underline{j}_2$ and $\underline{j}_3$ can be added to $\underline{j}_1$ to also give $\underline{J}$.

Then, if we use the notation of writing momenta that are coupled in brackets in front of the resultant, the unitary transformation between the two schemes above is :

$$\left|(j_1 j_2)j_{12}, j_3; JM\right\rangle = \sum_{j_{23}} \left|j_1, (j_2 j_3)j_{23}; JM\right\rangle \times \left\langle j_1, (j_2 j_3)j_{23}; JM \middle| (j_1 j_2)j_{12}, j_3; JM\right\rangle \tag{4.28}$$

The coefficients are independent of M, and are used to define the Wigner 6-j symbols.

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix} = (-1)^{j_1+j_2+j_3+J}\left[(2j_{12}+1)(2j_{23}+1)\right]^{-\frac{1}{2}}$$

$$\times \langle j_1,(j_2j_3)j_{23};JM|(j_1j_2)j_{12},j_3;JM\rangle \qquad (4.29)$$

Higher 3n-j symbols have been defined, but it is sufficient to define only the 9-j symbol which is used in the coupling of four momenta. Using the above notation to distinguish the order of coupling of momenta, the 9-j symbol is defined by :

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & J \end{Bmatrix} = \langle (j_1j_2)j_{12},(j_3j_4)j_{34};JM|(j_1j_3)j_{13},(j_2j_4)j_{24};JM\rangle$$

$$\times \left[(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)\right]^{-\frac{1}{2}} \qquad (4.30)$$

The properties of the 3n-j symbols are given in chapter 6 of Edmonds [1] and chapter 3 and appendices of Brink and Satchler [5].

## 4.6 Irreducible Spherical Tensor Operators

In three-dimensional space, the Cartesian tensors of a given rank are in general reducible under the operation of the full rotation group. For example, a general second rank tensor $T_{ij}$ can be split into the following :

$$T = \sum_i T_{ii} \;; \qquad A_{ij} = \tfrac{1}{2}(T_{ij} - T_{ji})$$

and $$S_{ij} = \tfrac{1}{2}(T_{ij} + T_{ji}) - \tfrac{1}{3}T \qquad (4.31)$$

These have respectively one, three and five independent components which transform amoung themselves on rotation and are irreducible components of the general second rank tensor and belong to the $\mathcal{D}_0$, $\mathcal{D}_1$ and $\mathcal{D}_2$ representations of the rotation group.

It is thus natural to define general spherical tensors $T^k_q$ of rank k which transform amoungst themselves like spherical harmonics if k is integral and form an irreducible representation $\mathcal{D}_k$ of the complete rotation group.

$$T^{k'}_q = \sum_p T^k_p \mathcal{D}^k_{pq}(\omega) \qquad (4.32)$$

where $T^{k'}_q$ expresses the $q^{th}$ component of $\underline{T}^k$ in new axes (those rotated by $(\alpha,\beta,\gamma)$ ) in terms of the old components $T^k_p$.

This is immediately extended to tensor operators, so that for operator $\underline{A}$ we obtain (just as in (4.13) and (4.14) ) :

$$\begin{aligned} T^{k'}_q(\underline{A}) &= D(\omega)\, T^k_q(\underline{A})\, D^{-1}(\omega) \\ &= \sum_p T^k_p(\underline{A}) \mathcal{D}^k_{pq}(\omega) \qquad (4.33) \end{aligned}$$

or the inverse :

$$T^k_p(\underline{A}) = \sum_q T^{k'}_q(\underline{A})\, \mathcal{D}^k_{pq}(\omega)^* \qquad (4.34)$$

An equivalent definition of spherical tensor operators is in terms of commutation relations. For an infinitesimal rotation $(1 - i\alpha J_\lambda)$,

$$\mathcal{D}^k_{pq}(\omega) = \delta_{pq} - i\alpha\langle kp|J_\lambda|kq\rangle$$

$$J_\lambda T^k_q - T^k_q J_\lambda = \sum_p T^k_p \langle kp|J_\lambda|kq\rangle$$

$$\left[J_z , T^k_q\right] = q\, T^k_q \tag{4.35}$$

$$\left[J_+ , T^k_q\right] = \left[k(k+1) - q(q+1)\right]^{\frac{1}{2}} T^k_{q+1} \tag{4.36}$$

## 4.7 Matrix Elements of Spherical Tensors

Consider the matrix element $\langle\alpha JM|T^k_q|\alpha' J'M'\rangle$ . The state vector $T^k_q|\alpha' J'M'\rangle$ transforms according to the $\mathcal{D}_k \times \mathcal{D}_{J'}$ representation, which is in general reducible and can be written as a sum of vectors with angular momentum KQ.

$$T^k_q\,|\alpha' J'M'\rangle = \sum_{K,Q} (-1)^{K-Q}(2K+1)^{-\frac{1}{2}}\begin{pmatrix} K & k & J' \\ -Q & q & M' \end{pmatrix}|\beta KQ\rangle \tag{4.37}$$

$$\langle\alpha JM|T^k_q|\alpha' J'M'\rangle = \sum_{K,Q} (-1)^{K-Q}\begin{pmatrix} K & k & J' \\ -Q & q & M' \end{pmatrix}(2K+1)^{-\frac{1}{2}} \times \langle\alpha JM|\beta KQ\rangle \tag{4.38}$$

$\langle\alpha JM|\beta KQ\rangle$ is non-zero only if J=K and M=Q and is also independent of M. Therefore we can rewrite (4.38) as :

$$\langle \alpha JM | T^k_q | \alpha' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \alpha J \| \underline{T}^k \| \alpha' J' \rangle \tag{4.39}$$

where $\langle \alpha J \| \underline{T}^k \| \alpha' J' \rangle$ is a reduced matrix element. The above result is known as the <u>Wigner-Eckart Theorem</u>, and basically states that a matrix element of a spherical tensor operator can be written as the product of a 3-j symbol and a term independent of the projection quantum numbers.

This can be extended to matrix elements in a coupled representation. Let two independent momenta $\underline{j}_1$ and $\underline{j}_2$ be coupled to give $\underline{J}$. For a tensor operator $T^k_q(1)$ or $T^k_q(2)$, which acts only on part 1 or part 2, we obtain :

$$\langle j_1' j_2 J' \| \underline{T}^k(1) \| j_1 j_2 J \rangle = (-1)^{j_1'+j_2+k_1+J} \left[(2J+1)(2J'+1)\right]^{\frac{1}{2}} \times \begin{pmatrix} j_1' & J' & j_2 \\ J & j_1 & k_1 \end{pmatrix} \langle j_1' \| \underline{T}^k(1) \| j_1 \rangle \tag{4.40}$$

$$\langle j_1 j_2' J' \| \underline{T}^k(2) \| j_1 j_2 J \rangle = (-1)^{j_1+j_2'+k_2+J'} \left[(2J+1)(2J'+1)\right]^{\frac{1}{2}} \times \begin{pmatrix} j_2' & J' & j_1 \\ J & j_2 & k_2 \end{pmatrix} \langle j_2' \| \underline{T}^k(2) \| j_2 \rangle \tag{4.41}$$

In certain circumstances, the tensor operator $\underline{T}^k$ is formed by the reduction of the product of two other tensor operators $\underline{T}^{k_1}$ and $\underline{T}^{k_2}$. That is :

$$T^K_Q(k_1,k_2) = \sum_q T^{k_1}_q \, T^{k_2}_{Q-q} \, (-1)^{K-Q}(2K+1)^{-\frac{1}{2}} \begin{pmatrix} K & k_1 & k_2 \\ -Q & q & Q-q \end{pmatrix} \quad (4.42)$$

Then with the above coupled wavefunctions, the matrix elements can be re-written as :

$$\left\langle j_1'j_2'J' \left\| \underline{T}^K(k_1,k_2) \right\| j_1j_2J \right\rangle = \left[(2J+1)(2J'+1)(2K+1)\right]^{\frac{1}{2}} \begin{Bmatrix} j_1' & j_1 & k_1 \\ j_2' & j_2 & k_2 \\ J' & J & K \end{Bmatrix}$$

$$\times \left\langle j_1' \left\| \underline{T}^{k_1} \right\| j_1 \right\rangle \left\langle j_2' \left\| \underline{T}^{k_2} \right\| j_2 \right\rangle \quad (4.43)$$

A special example of this is the scalar product of two tensor operators; this may be obtained by K=0 and $k_1=k_2=k$. Then :

$$\left\langle j_1'j_2'J'M' \left| \underline{T}^k(1).\underline{T}^k(2) \right| j_1j_2JM \right\rangle = (-1)^{j_1+j_2'+J} \begin{pmatrix} J & j_2' & j_1' \\ k & j_1 & j_2 \end{pmatrix} \delta_{JJ'}\delta_{MM'}$$

$$\times \left\langle j_1 \left\| \underline{T}^k(1) \right\| j_1 \right\rangle \left\langle j_2 \left\| \underline{T}^k(2) \right\| j_2 \right\rangle \quad (4.44)$$

## References to Chapter 4

1. A. R. Edmonds, "Angular Momentum in Quantum Mechanics", (Princeton University Press, 1957).

2. E. P. Wigner, "Group Theory and its Application to Quantum Mechanics of Atomic Spectra", (Academic Press, New York, 1959).

3. U. Fano and G. Racah, "Irreducible Tensorial Sets", (Academic Press, New York, 1959).

4. M. E. Rose, "Multipole Fields", (Oxford University Press, 1955).

5. D. M. Brink and G. R. Satchler, "Angular Momentum", (Oxford University Press, 1968).

6. A. Messiah, "Quantum Mechanics", (North-Holland Publishing Co., Amsterdam, 1965).

7. M. E. Rose, "Elementary Theory of Angular Momentum", (John Wiley and Sons, Inc., 1957).

8. E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra", (Cambridge University Press, 1935).

9. H. Marganau and G. M. Murphy, "The Mathematics of Physics and Chemistry", (van Nostrand, Co Ltd., 1956).

# Chapter 5

# AN EFFECTIVE HAMILTONIAN AND ITS MATRIX ELEMENTS FOR A LINEAR MOLECULE

## 5.1 Introduction

In this chapter, we shall formulate a scheme for the calculation of the energy levels of open-shell molecules. The method of approach is that for diatomic molecules, but can be readily modified to account for more complicated systems, for example linear triatomic molecules which will be considered later.

## 5.2 Born-Oppenheimer Approximation

The exact wave-function to describe a molecule is difficult to obtain; instead approximate methods can be used to calculate the energy levels.

First of all, it is necessary to adopt a basis, for calculating the matrix elements, which most closely approximates to the exact wave-function of the physical system.

The vast difference in velocities of nuclei and electrons (a factor of about $10^4$) allows a separation of their motions. This was performed in a classic paper by Born and Oppenheimer [1,2] who showed that to a good approximation the total wave-function for a diatomic molecule can be written as the product of a rotational part, a vibrational part, and an electronic part. Thus,

$$\Psi = \psi_{el}\,\psi_{vib}\,\psi_{rot} \tag{5.1}$$

Let us now consider the simple field free case in the absence of magnetic interactions between particles, where the Hamiltonian is:

$$\mathcal{H} = \frac{P^2}{2M} + B\,(\underline{J} - \underline{W})^2 + \sum_r P_r^2 + \sum_i \frac{1}{2m}\,p_i^2 + \frac{1}{2M_N}\left(\sum_i \underline{p}_i\right)^2 + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - \sum_{\alpha,i} \frac{Z_\alpha e^2}{r_{i\alpha}} \tag{5.2}$$

The translational motion is completely separable and will not be considered further; it just shifts the energy zero by an amount not detectable spectroscopically. By expanding both the wave-function and the Hamiltonian in a power series of $(m/M)^{\frac{1}{4}}$, Born and Oppenheimer [1] showed that the best electronic wave-function is obtained by solving the Hamiltonian for electronic motion at each internuclear distance. This assumes the previously stated fact that the electronic motion is much faster than the nuclear motion and that consequently the electronic motion and hence wave-function responds instantaneously to the change in nuclear configuration. Hence the electronic wave-function, which is also a function of vibrational coordinates, is obtained by solving :

$$\mathcal{H}_e \psi_e^s(\underline{r}_i, Q_r) = \left[ \sum_i \frac{1}{2m} p_i^2 + \frac{1}{2M_N} \left( \sum_i \underline{p}_i \right)^2 + \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_{\alpha, i} \frac{Z_\alpha e^2}{r_{i\alpha}} \right] \psi_e^s(\underline{r}_i, Q_r)$$

$$= E_e^s(Q_r)\, \psi_e^s(\underline{r}_i, Q_r) \qquad (5.3)$$

where $\underline{r}_i$ and $Q_r$ are electronic and vibrational normal coordinates respectively.

In the case of a diatomic or a linear polyatomic molecule in its linear equilibrium configuration, rotation of the electrons about the molecule-fixed z axis leaves the Hamiltonian unchanged. Hence the z component of the total orbital angular momentum operator commutes with $\mathcal{H}_e$ and the electronic wave-function is an eigenfunction of $L_z$ with eigenvalue $\Lambda$. This is not true when the molecule leaves its linear configuration, since coupling between electronic and vibrational motion destroys $\Lambda$ as a good quantum number. The problem of the linear triatomic molecule is considered in chapter 8. Here we shall limit ourselves to the easier diatomic species although much of the reasoning is easily extended to other systems.

The electron spin will also be considered to be quantised along the molecular z-axis. This yields Hund's coupling case a, which closely approximates the truth in the molecules considered in this dissertation (all $^2\Pi$); their spin-orbit coupling constants are many times the rotational constants. See, for example, Herzberg [3] for details of the coupling schemes. The component of total spin angular momentum, $S_z$, along the molecular z-axis is thus a good quantum number. The total electronic wave-function will now be written in the form $\psi_e^s(\Lambda,\Sigma;\underline{r}_i,Q_r)$ to emphasise it is an eigenfunction of $L_z$ and $S_z$; it is also an eigenfunction of $P_z$ (with eigenvalue $\Omega$ ) the z component of the total electronic angular momentum, $\underline{P} = \underline{L} + \underline{S}$.

Since these electronic wave-functions form a complete set, the total wave-function, $\Psi$, can be written as a sum of products of $\psi_e^s$ with a nuclear wave-function $F_n^s(Q_r,\theta,\phi,\chi)$; the rotational and vibrational motions have not yet been seperated but are considered together as nuclear motions (all the arguements of $F_n^s$ are specified by the nuclear coordinates). Then :

$$\Psi = \sum_s \psi_e^s(\Lambda,\Sigma;\underline{r}_i,Q_r)\, F_n^s(Q_r,\theta,\phi,\chi) \tag{5.4}$$

and

$$\mathcal{H}\Psi = E\Psi \tag{5.5}$$

Premultiplying by $\psi_e^{t*}$ and integrating over all electronic coordinates $d\tau$ (including spin) yields :

$$\left\{B(J^2 - \Omega^2) + \tfrac{1}{2}\sum_r P_r^2 + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + E_e^s(Q_r) + C_{ss} - E\right\} F_n^s$$

$$= -\sum_{t\neq s} C_{st}\, F_t(Q_r,\theta,\phi,X) \qquad (5.6)$$

where

$$C_{ss} = \int \psi_e^{s*} \sum_r \tfrac{1}{2}(P_r^2\, \psi_e^s)\, d\tau + \int \psi_e^{s*} B(P_x^2 + P_y^2)\, \psi_e^s d\tau \quad (5.7)$$

$$C_{st} = -\int \psi_e^{t*}\, 2B(P_x J_x + P_y J_y)\, \psi_e^s\, d\tau \qquad (5.8)$$

In the Born-Oppenheimer approximation, all the C's were neglected (they contributed in the next order of $(m/M)^{\frac{1}{4}}$ ). The Born adiabatic approximation [2], however, is more precise and includes the diagonal matrix elements $C_{ss}$, while still neglecting $C_{st}$. The wave-functions are still simple products of nuclear and electronic functions and it can be shown using the Variational Principle (see, for example, Longuet-Higgins [4]) that this is the best product wave-function with $\psi_e$ obeying (5.3), i.e. the best approximation in which the electrons follow the nuclear motion adiabatically.

In (5.6), the rotational and vibrational variables are readily separable (on division by B), so that $F_n$ can be written exactly as the product of a vibrational and a rotational wave-function.[5]

$$F_n(Q_r,\theta,\phi,\chi) = V(Q_r)\ R(\theta,\phi,\chi) \tag{5.9}$$

where,

$$(J^2 - \Omega^2)\ R(\theta,\phi,\chi) = E_{rot}/B\ R(\theta,\phi,\chi) \tag{5.10}$$

and

$$\left(\sum_r \tfrac{1}{2}P_r^2 + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + E_e^s(Q_r) + C_{ss} + E_{rot}\right) V(Q_r) = E\ V(Q_r) \tag{5.11}$$

The rotational eigen-equation is that for a symmetric top, with solutions :

$$Z(\theta,\phi,\chi) = \left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^J_{M\Omega}(\theta,\phi,\chi)^* \tag{5.12}$$

where $\mathcal{D}^J_{M\Omega}(\omega)$ 6,7 is the rotation matrix defined in (4.14). It is an eigenfunction of $\underline{J}^2$, $J_Z$, and $J_z$ (where we use upper and lower case letters for respectively space and molecule-fixed components) with eigenvalues $J(J+1)$, $M$ and $\Omega$, respectively.

The vibrational equation can be written as a power series in nuclear displacements from the equilibrium configuration (at the potential minimum). All first power terms are zero and the quadratic terms are written in terms of the normal coordinates, $Q_r$, which are chosen such that no cross terms exist. One usually chooses basis vibrational wave-functions as those that satisfy the quadratic potential. Each normal mode is now separable yielding a product wave-function, with each individual component obeying :

$$\left( \tfrac{1}{2}P_r^2 + \tfrac{1}{2}k_r Q_r^2 \right) \chi_n(Q_r) = E_n \chi_n(Q_r) \qquad (5.13)$$

The solutions are :

$$\chi_n(Q_r) = (\sqrt{\pi}\, 2^n n!\,)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}\, k_r Q_r^2)\; H_n(k_r^{\frac{1}{4}} Q_r) \qquad (5.14)$$

where, $H_n(x)$ is a Hermite polynomial,

$$H_n(x) = (-1)^n \exp x^2 \; \frac{d^n}{dx^n} \exp(-x^2) \qquad (5.15)$$

The total wave-function is then written as :

$$\Psi = \psi_s(\Lambda,\Sigma;\underline{r}_i,Q_r) \left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} \mathfrak{D}^{J}_{M\Omega}(\omega)^{*} \prod_r \chi_r(Q_r) \qquad (5.16)$$

This type of wave-function will be used as the "best" approximate solution to the complete wave-function, even when external fields and magnetic interactions between particles are included. If nuclear spins are also considered, the above wave-function must be multiplied by the appropriate nuclear spin functions (spins assumed space-quantised). If coupling to the nuclear frame is sufficiently great to give a molecule quantised spin, in the rotational wave-function must be considered to also contain the nuclear spin momentum as must $\underline{W}$ in the rotational Hamiltonian (cf electron spin)

## 5.3 Effective Hamiltonian for a Diatomic Molecule

In the following chapters, we shall be studying the spectra of molecules in their ground electronic and usually ground vibrational state. Many terms in the Hamiltonian mix in excited vibrational and electronic states, but they are of a sufficiently small magnitude that their effects can be adequately treated by second order perturbation theory. This approach has been used by Tinkham and Strandberg [8] and Rosenblum, Nethercot and Townes [9]. A more pleasing approach is to modify the Hamiltonian in such a way that when it acts in just the ground vibronic state it gives the same energies as the complete Hamiltonian acting in the complete manifold of states, i.e. an effective Hamiltonian is formed.

From now on, the translational motion of the molecule as a whole will be neglected. The initial 'basis' wave-functions are determined according to the method of Born and Oppenheimer [1] or Born and Huang [2]. Let us now allow the electronic Hamiltonian (5.1) to also include the orbit-orbit interactions (3.212) and (3.213); it can then be solved to give the electronic wave-function $\psi_e^s(\Lambda,\Sigma;\underline{r}_i,Q_r)$. The energy, $E_e^s$, essentially fixes the energy of each electronic state.

Most of the important terms in the total molecular Hamiltonian are diagonal in the electronic state. The remaining non-adiabatic terms like $C_{st}$ in (5.8) are the ones which will be included in our effective Hamiltonian by second order perturbation theory.

If the potential energy is expressed as a power series in $Q_r$, the total Hamiltonian (after letting $E_e^s(0)$ be the electronic energy at $Q_r = 0$ for a given electronic state) is given by :

$$\mathcal{H} = E_e^s(0) + \sum_r \tfrac{1}{2}P_r^2 + V(Q_r) + B(\underline{J} - \underline{L} - \underline{S})^2$$

$$+ \mathcal{H}_{so} + g_s\beta\,\underline{H}.\underline{S} + g_L\beta\,\underline{H}.\underline{L} + \mathcal{H}'' \qquad (5.17)$$

where $\mathcal{H}_{so}$ is the spin-orbit interaction and $\mathcal{H}''$ contains the following small terms :

$$\mathcal{H}'' = \mathcal{H}_{ss} + \mathcal{H}_{hyp} + \mathcal{H}_{quad} + \mathcal{H}_{NZ} + \mathcal{H}_{RZ}$$

$$+ \mathcal{H}_{SR} + \mathcal{H}_{LR} + \mathcal{H}_{E} \qquad (5.18)$$

These are, respectively, the electron spin-spin, hyperfine, quadrupole, nuclear Zeeman, rotational Zeeman, spin-rotation, orbit-rotation and electric field (Stark) interactions.

The spin-orbit interaction is often written phenomenologically as $A\underline{L}.\underline{S}$ [10]; this is usually sufficiently accurate to describe electronic spectra, but more care must be taken here about its form. The true spin-orbit Hamiltonian (3.210) and (3.211) can be written as a tensor coupling between the orbital angular momentum of electron i and the electron spin of electron j. As was demonstrated by Kayama and Baird [11], $A\underline{L}\cdot\underline{S}$ allows mixing of states with $\Delta\Lambda=\pm1, \Delta\Sigma=\mp1$, but omits all interactions in which the total spin can be changed by 1. Here we shall use the short-hand form $\sum_i (a_i \underline{l}_i)\cdot\underline{s}_i$ which gives the correct selection rules on matrix elements between electronic states; it cannot, however, be used in the calculation of spin-orbit coupling constants from wave-functions where the more precise Hamiltonian (3.210) and (3.211) must be used. A different treatment of the matrix elements of the exact spin-orbit term (without mass-polarization corrections) has been given by Fontana and Meath [12].

The terms $\mathcal{H}''$ are sufficiently small or have small enough matrix elements between electronic states that their second order mixing of excited states may be neglected. The remaining terms, $\mathcal{H}' = \mathcal{H} - \mathcal{H}''$, yield significant mixing. Then, including the second order contributions by degenerate perturbation theory [13,14], the effective Hamiltonian is given by :

$$\mathcal{H}_{eff} = P_o \mathcal{H} U = P_o \mathcal{H} P_o + P_o \mathcal{H}' \frac{Q_o}{a} \mathcal{H}' P_o \qquad (5.19)$$

where $P_o$ is the projection operator onto the ground electronic state $\ell_o$ :

$$P_o = \sum_k |\ell_o k\rangle\langle \ell_o k| \qquad (5.20)$$

where k represents all other relevant quantum numbers necessary to specify the state. $Q_o$ is the projection operator onto all other electronic states $\ell_n$ such that :

$$\frac{Q_o}{a^r} = \sum_{\ell_n \neq \ell_o} \sum_k \frac{|\ell_n k\rangle\langle \ell_n k|}{(E_o - E_n)^r} \tag{5.21}$$

$E_n - E_o$ is the difference in electronic energies between the ground and excited states.

If $\mathcal{H}'$ is now expanded in terms of spherical tensor operators [15,16] measured with respect to the molecule-fixed axis system :

$$\begin{aligned}\mathcal{H}' = {} & \sum_r \tfrac{1}{2}P_r^2 + V(Q_r) + B\left[\underline{T}^1(\underline{J}).\underline{T}^1(\underline{J}) - 2\underline{T}^1(\underline{J}).\underline{T}^1(\underline{S})\right] \\ & + B\left[\underline{T}^1(\underline{S}).\underline{T}^1(\underline{S}) + \underline{T}^1(\underline{L}).\underline{T}^1(\underline{L}) - 2T_0^1(\underline{L})^2\right] \\ & + \sum_i T_0^1(a_i\underline{l}_i)T_0^1(\underline{s}_i) + \sum_q (-1)^q\Big\{T_q^1(\underline{L})\Big[2B\,T_{-q}^1(\underline{S}) \\ & \qquad - 2B\,T_{-q}^1(\underline{J}) + g_L\beta\,T_{-q}^1(\underline{H})\Big]\sum_i T_{-q}^1(a_i\underline{l}_i)\;T_q^1(\underline{s}_I)\Big\}\end{aligned} \tag{5.22}$$

with q = ±1.

The most important contributions in second order are those between electronic states in which $\Lambda$ has been changed by 1, and the perturbation originates and ends in the same component of the ground electronic state (for $\Lambda \neq 0$, the electronic state is doubly degenerate). Then taking all combinations of terms from (5.22) one obtains :

$$\mathcal{H}'_{\mathrm{eff}} = P_o\Big\{ \lambda'' T^2_0(\underline{S}) + B''\Big[\underline{T}^1(\underline{J})\cdot\underline{T}^1(\underline{J}) - T^1_0(\underline{J})T^1_0(\underline{J})\Big] + \mathcal{L}''\beta^2 T^2_0(\underline{H})$$

$$+ \sum_q (-1)^q \Big[2(\gamma'' - B'')T^1_q(\underline{J})T^1_{-q}(\underline{S}) + \Delta g_s \beta\, T^1_q(\underline{H})T^1_{-q}(\underline{S})$$

$$+ g^e_r \beta T^1_q(\underline{H})T^1_{-q}(\underline{J}-\underline{S})\Big] \quad + \quad \mathrm{const}\Big\} P_o \qquad (5.23)$$

where, $$\lambda'' = -\sum_{\ell_n} (6)^{-\frac{1}{2}} \sum_q (E_n - E_o)^{-1} \langle \ell_o | (A+2B)T^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | (A+2B)T^1_{-q}(\underline{L}) | \ell_o \rangle \qquad (5.24)$$

Here, since S has not been changed, we are allowed to replace $\sum_i T^1_q(a_i \underline{l}_i)T^1_{-q}(\underline{s}_i)$ by $AT^1_q(\underline{L})T^1_{-q}(\underline{S})$, after a suitable choice of A (cf. $\gamma''$ and $\Delta g$).

$$B'' = \sum_n \sum_q -2(E_n - E_o)^{-1} \langle \ell_o | BT^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | BT^1_{-q}(\underline{L}) | \ell_o \rangle \qquad (5.25)$$

$$\mathcal{L}'' = -(6)^{-\frac{1}{2}} \sum_n \sum_q (E_n - E_o)^{-1} \langle \ell_o | g_L T^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | g_L T^1_{-q}(\underline{L}) | \ell_o \rangle \qquad (5.26)$$

$$g^e_r = -\sum_n \sum_q g_L (E_n - E_o)^{-1} \Big\{ \langle \ell_o | BT^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | T^1_{-q}(\underline{L}) | \ell_o \rangle$$

$$+ \langle \ell_o | T^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | BT^1_{-q}(\underline{L}) | \ell_o \rangle \Big\} \qquad (5.27)$$

$$\gamma'' = \sum_n \sum_q -\tfrac{1}{2}(E_n-E_o)^{-1}\Big\{\langle \ell_o|(A+2B)T^1_q(\underline{L})|\ell_n\rangle\langle \ell_n|BT^1_{-q}(\underline{L})|\ell_o\rangle$$
$$+ \langle \ell_o|BT^1_q(\underline{L})|\ell_n\rangle\langle \ell_n|(A+2B)T^1_{-q}(\underline{L})|\ell_o\rangle\Big\} \tag{5.28}$$

$$\Delta g_s = \sum_n \sum_q \tfrac{1}{2}g_L(E_n-E_o)^{-1}\Big\{\langle \ell_o|AT^1_q(\underline{L})|\ell_n\rangle\langle \ell_n|T^1_{-q}(\underline{L})|\ell_o\rangle$$
$$+ \langle \ell_o|T^1_q(\underline{L})|\ell_n\rangle\langle \ell_n|AT^1_{-q}(\underline{L})|\ell_o\rangle\Big\} \tag{5.29}$$

Note that all the corresponding terms given in the work of Carrington, Currie, Levy and Miller [17,18] are a factor of two too large.

The parts of (5.23) give, respectively, the second order corrections : $\lambda''$ to the electron spin-spin interaction, $B''$ to the rotational constant, $\mathcal{L}''$ to the high frequency paramagnetism, $g_r^e$ is the electronic contribution to the rotational Zeeman effect, $\gamma''$ to the spin-rotation interaction and $\Delta g_s$ is an anisotropic contribution to the electron g-value.

In a doublet state, such as $^2\Pi$ which we shall mainly be considering, the spin-spin interaction term disappears, since a second rank tensor operator cannot give non-zero matrix elements between $S=\frac{1}{2}$ states (i.e. vectors of length $\frac{1}{2},\frac{1}{2}$ and 2 cannot form a triangle).

Further second order contributions from excited states with the same value of $\Lambda$ and diagonal in $\underline{S}^2$ yield :

$$\mathcal{H}^2_{\text{eff}} = P_o\Big\{\bar{\lambda}''T^2_0(\underline{S}) + \bar{B}''(\underline{J}-\underline{L}-\underline{S})^2 + \bar{D}''(\underline{J}-\underline{L}-\underline{S})^4 + \bar{V}''(Q_r)$$

$$+ \bar{A}''T^1_0(\underline{L})T^1_0(\underline{S}) + \bar{\Xi}''(\underline{J}-\underline{L}-\underline{S})^2T^1_0(\underline{L})T^1_0(\underline{S})\Big\}P_o \tag{5.30}$$

where :

$$\bar{\gamma}'' = \sum_n -(\tfrac{2}{3})^{\frac{1}{2}}\,(E_n-E_o)^{-1}\,\langle \ell_o|AT^1_0(\underline{L})|\ell_n\rangle\langle \ell_n|AT^1_0(\underline{L})|\ell_o\rangle \tag{5.31}$$

$$\bar{B}'' = \sum_n -\,(E_n-E_o)^{-1}\Big\{\langle \ell_o|B|\ell_n\rangle\langle \ell_n|\bar{V}(Q_r)\,|\,\ell_o\rangle$$

$$+ \langle \ell_o|\bar{V}(Q_r)|\ell_n\rangle\langle \ell_n|B\,|\,\ell_o\rangle\Big\} \tag{5.32}$$

$$\bar{D}'' = \sum_n -\,(E_n-E_o)^{-1}\,\langle \ell_o\,|\,B\,|\ell_n\rangle\langle \ell_n\,|\,B\,|\,\ell_o\rangle \tag{5.33}$$

$$\bar{A}'' = \sum_n -\,(E_n-E_o)^{-1}\Big\{\langle \ell_o|A|\ell_n\rangle\langle \ell_n|\bar{V}(Q_r)\,|\,\ell_o\rangle$$

$$+ \langle \ell_o|\bar{V}(Q_r)|\ell_n\rangle\langle \ell_n|A|\,\ell_o\rangle\Big\} \tag{5.34}$$

$$\bar{\Xi}'' = \sum_n -\,(E_n-E_o)^{-1}\Big\{\langle \ell_o\,|\,A\,|\,\ell_n\rangle\langle \ell_n\,|\,B\,|\,\ell_o\rangle$$

$$+ \langle \ell_o\,|\,B\,|\,\ell_n\rangle\langle \ell_n\,|\,A\,|\,\ell_o\rangle\Big\} \tag{5.35}$$

$$V''(Q_r) = \sum_n -(E_n-E_o)^{-1}\langle \ell_o|\bar{V}(Q_r)|\ell_n\rangle\langle \ell_n|\bar{V}(Q_r)|\ell_n\rangle \tag{5.35}$$

with $\bar{V}\,(Q_r)$ used to represent the vibrational Hamiltonian $\sum_r \frac{1}{2}P_r^2 + V(Q_r)$ $\bar{\gamma}''$, $\bar{B}''$ and $\bar{A}''$ are small contributions to the spin-spin dipolar interaction, the rotational constant and the spin-orbit coupling constant. $\bar{\Xi}''$ is an unusual term which tends to give different rotational constants in the different fine-structure components of a particular electronic (or vibronic) state. This might invalidate some of the work on the determination of spin-orbit coupling constants from the measurements of effective rotational constants [19,20]. For example, in $^2\Pi$ molecules use is made of $B_{eff} = B(1 \pm B/A)$.

The parts of the spin-orbit coupling which can connect electronic states of different multiplicity give a second order contribution :

$$\mathcal{H}^3_{eff} = \sum_n \sum_q - (E_n - E_o)^{-1} \sum_{i,j} \langle \ell_o | T^1_q(a_i \underline{l}_i) | \ell_n \rangle \langle \ell_n | T^1_{-q}(a_j \underline{l}_j) | \ell_o \rangle$$
$$\times \; T^1_q(\underline{s}_j)\, T^1_{-q}(\underline{s}_i) \qquad (5.36)$$

which when operating in a state of given multiplicity can be replaced by :

$$\mathcal{H}^3_{eff} = \bar{\bar{\lambda}}''' \, T^2_0(\underline{S}) \qquad (5.37)$$

This will not affect the spectrum of a molecule in a doublet state and together with the remaining terms of the same form will be omitted from the Hamiltonian for the study of $^2\Pi$ molecules. This term, however, has been found to be important in the interpretation of triplet state molecules like $^3\Sigma$ oxygen [21].

The resulting Hamiltonian acts only within the ground electronic state. It is desirable to further reduce the Hamiltonian to one acting only in the ground vibrational state.

The non-diagonal part of the vibrational energy $(\sum_r \frac{1}{2}P_r^2 + V(Q_r))$ strongly mixes the various vibrational states. Its second order contribution modifies slightly the energy of a particular vibrational level. Its cross-terms with all the other quantities in the effective Hamiltonian which can mix vibrational levels slightly modifies these terms but keeps them of the same form. Thus from a typical term of the form $\mathcal{B}\,\underline{T}^1(\underline{M}).\underline{T}^1(\underline{N})$ one obtains an additional term : $\mathcal{B}''\underline{T}^1(\underline{M}).\underline{T}^1(\underline{N})$ where

$$\mathcal{B}'' = \sum_v - (E_v - E_o)^{-1}\Big\{\langle \ell_o|\mathcal{B}|\ell_v\rangle\langle\ell_v|\bar{V}(Q_r)|\ell_o\rangle + \langle\ell_o|\bar{V}(Q_r)|\ell_v\rangle\langle\ell_v|\mathcal{B}|\ell_o\rangle\Big\} \qquad (5.38)$$

The cross-terms between these latter quantities will in general be neglected. Their coefficients normally have only weak vibrational dependence, so mixing of excited vibrational states will be slight. Amoung these is the rotational term quadratic in rotational quantum number J (rotational distortion term); it is typically of the order of $10^{-3}$ cm$^{-1}$ and has a completely negligible effect on gas-phase e.p.r.

spectra. All the major Zeeman terms have negligible vibrational dependence, so that the Hamiltonian in a particular vibronic level can be written as :

$$\begin{aligned}\mathcal{H} = P_o\Big\{ & B'(\underline{J}-\underline{L}-\underline{S})^2 + g_s\beta\,\underline{H}\cdot\underline{S} + g_L\beta\,T^1_0(\underline{L})T^1_0(\underline{H}) + A'T^1_0(\underline{L})T^1_0(\underline{S}) \\ & + \sum_q(-1)^q\Big[\Delta g_s\beta\,T^1_q(\underline{H})T^1_{-q}(\underline{S}) + \gamma' T^1_q(\underline{J}-\underline{S})T^1_{-q}(\underline{S}) \\ & \qquad + g_r\beta\,T^1_q(\underline{H})T^1_{-q}(\underline{J}-\underline{S})\Big] + \lambda' T^2_0(\underline{S}) + \mathcal{L}' T^2_0(\underline{H}) \\ & + \mathcal{H}_{hyp} + \mathcal{H}_{quad} + \mathcal{H}_{NZ} + \mathcal{H}_E\Big\}P_o \qquad (5.39)\end{aligned}$$

with
$$B' = B + \breve{B}'' + \bar{B}'' + B''' \qquad (5.40)$$

where the term with triple dashes signifies that obtained by second order mixing of vibrational states in an analogous manner to the mixing of electronic states in (5.24) to (5.29).

Also :
$$\lambda' = \lambda + \lambda'' + \bar{\lambda}'' + \bar{\bar{\lambda}}'' + \lambda''' \qquad (5.41)$$

where $\lambda$ includes the diagonal contribution of the electron-electron dipolar spin-spin interaction from (3.214),

$$g_r = g^e_r - g^n_r \qquad (5.42)$$

with the nuclear contribution, $g^n_r$, obtained by expanding (3.203), $\Delta g_s$ is essentially that given in (5.29) ,

$$A' = A + A'' + \bar{A}'' \tag{5.43}$$

and

$$\gamma' = \gamma + \gamma'' + \bar{\gamma}'' \tag{5.44}$$

where $\gamma$ is the expectation value of the coefficient of $\underline{N}.\underline{S}$ in (3.211). The analogous orbit-rotation term from (3.213) has a zero coefficient.

$\Xi'' T^1_0(\underline{S}) T^1_0(\underline{L})\ (\underline{J}-\underline{L}-\underline{S})^2$ can be neglected since we shall be working in just one fine structure state and we shall use the rotational constant appropriate to that state.

In a $\Pi$ electronic state with $\Lambda = \pm 1$, it is possible to mix the two components in second order perturbation theory. This will remove the degeneracy of the two components giving rise to what is known as $\Lambda$-doubling [3] or in the case of good Hund's case (a) molecules, $\Omega$-type doubling. This results from the fact that, in the absence of external electric fields, the complete Hamiltonian is invariant to space-inversion (i.e. $\mathcal{H}$ commutes with the inversion operator $\mathcal{J}$). Therefore the eigenfunctions of the Hamiltonian can correspondingly be written as eigenfunctions of $\mathcal{J}$.

Now as demonstrated by Hougan [21] and Chiu [22], upon inversion of all particles in the space-fixed axes, the Euler angles $(\alpha,\beta,\gamma)$ specifying the orientation of the molecular axis system change as follows :

$$\alpha \rightarrow \pi + \alpha \ ; \quad \beta \rightarrow \pi - \beta \ ; \quad \gamma \rightarrow -\gamma \tag{5.45}$$

Therefore making use of the properties of the rotation matrices $\mathcal{D}^{k}_{pq}(\omega)$, namely :

$$\left[\mathcal{D}^{J}_{M\Omega}(\alpha\beta\gamma)\right]^{*} = e^{iM\alpha}\left[d^{J}_{M\Omega}(\beta)\right]^{*}e^{i\Omega\gamma} \tag{5.46}$$

and

$$\left[d^{J}_{M\Omega}(\pi-\beta)\right]^{*} = (-1)^{J-M}\left[d^{J}_{M-\Omega}(\beta)\right]^{*}, \tag{5.47}$$

the rotational wave-functions transforms as :

$$\mathcal{I}\ \mathcal{D}^{J}_{M\Omega}(\alpha\beta\gamma)^{\,*} = (-1)^{J}\ \mathcal{D}^{J}_{M-\Omega}(\alpha\beta\gamma)^{\,*} \tag{5.48}$$

The spin wave-functions can be treated similarly :

$$|S\Sigma\rangle = \sum_{M_S}|SM_S\rangle\,\mathcal{D}^{S}_{M_S\Sigma}(\alpha\beta\gamma) \tag{5.49}$$

$$\mathcal{I}\,|S\Sigma\rangle = (-1)^{-S}\sum_{M_S}|SM_S\rangle\ \mathcal{D}^{S}_{M_S-\Sigma}(\alpha\beta\gamma) \tag{5.50}$$

$$= (-1)^{-S}\ |S\ -\Sigma\rangle \tag{5.51}$$

Upon inversion, the electronic coordinates transform as :

$$x_i \rightarrow -x_i\ ,\quad y_i \rightarrow y_i\ ,\quad z_i \rightarrow z_i \tag{5.52}$$

Therefore, the angular coordinate of an electron $\theta_i$ in cylindrical polar coordinates goes to $-\theta_i$. Thus representing the vibronic wave-function by $|\eta_o\Lambda\rangle$,

$$\mathcal{I}\,|\eta_o\Lambda\rangle = |\eta_o\ -\Lambda\rangle \tag{5.53}$$

Hence,

$$\mathcal{I}\,|\eta_o\Lambda J\Omega S\Sigma M_J\rangle = (-1)^{J-S}|\eta_o{-\Lambda}S{-\Sigma}J{-\Omega}M_J\rangle \tag{5.54}$$

The phase here differs from that of Hougan [23] because of his unusual definition of the phase of his wave-functions. However the phase obtained by many other authors [24,25] who use the phase convention of Condon and Shortley [26] and rotational wave-functions with the same phase as the rotation matrices [6] should be modified. The true wave-functions are then :

$$\psi_{\pm} = |\eta_o \Lambda S \Sigma J \Omega M_J\rangle \pm (-1)^{J-S} |\eta_o -\Lambda S -\Sigma J -\Omega M_J\rangle \qquad (5.55)$$

where we take the + or - sign, according to whether we want the + or - parity state.

The $\Omega$-doubling properties between these states has been considered by Lucas [25], but does not affect us here since in the molecules to be considered, the $\Omega$-doubling has not been observed. In the absence of the $\Omega$-doubling terms, the matrix elements of the effective Hamiltonian are necessarily the same for both components of the $\Omega$-doublet. These in turn are equal to the matrix elements in the representation $|\eta_o \Lambda S \Sigma J \Omega M_J\rangle$ which does not possess inversion symmetry. We shall, however, find it convenient to use this last representation for the calculation of matrix elements.

## 5.4 Matrix Elements

Since the basis functions involve the coupling of many momenta, it is desirable to use the techniques of spherical tensor operators [6,27], which simplifies the evaluation of matrix elements.

The case (a) basis set $|\eta_o \Lambda S \Sigma J \Omega M_J I M_I\rangle$ with a decoupled nuclear spin, very closely approximates to the true physical situation. However, $M_J$ and $M_I$ are not completely good quantum numbers and it is often found convenient in matrix diagonalization to use a coupled representation $|\eta_o \Lambda S \Sigma I J \Omega F M_F\rangle$ with $\underline{I}$ and $\underline{J}$ coupled to give a total angular momentum $\underline{F}$, and where $M_F$, the space z-component of $\underline{F}$, is a good quantum number. Below the matrix elements of the complete effective Hamiltonian will be evaluated in both the coupled and decoupled representations.

### 5.4.1 Anomalous Commutation Relationships of J

If the rotational angular momentum is referred to the molecule-fixed axes, it is found that its components do not obey normal commutation relations [28] but have the sign of i reversed.

$$\left[J_x\ ,\ J_y\right] \ = \ -iJ_z \qquad \text{and cyclic} \qquad (5.56)$$

This results from the fact that the components of $\underline{J}$ do not commute with the direction cosines, relating one axis system to the other [28].

It is thus not readily possible to expand a scalar product of $\underline{J}$ with some other vector in terms of spherical tensor operators in the molecule-fixed axis system. This is related to the fact that true spherical tensors are defined via normal commutation relationships. Van Vleck got around this problem by devising the method of reversed angular momentum. He could have reversed $\underline{J}$ so that $\underline{\tilde{J}} = -\underline{J}$ obeys normal commutation relations. Instead he reversed all normal momenta so that they commuted with an anomalous sign.

$$\text{i.e.}\quad \underline{\tilde{P}} = -\underline{P} \quad \text{gives} \quad \left[\tilde{P}_x , \tilde{P}_y\right] = -i\tilde{P}_z \tag{5.57}$$

The arbitrary phase in the matrix elements was chosen so that $J_x$ gave real and positive (and consequently $\tilde{J}_x$ gave real and negative) matrix elements. This is in disagreement with the phase convention of Condon and Shortley [26] which is almost universally used.

With the definition of rotation matrices, it is possible to write the Hamiltonian in terms of space-fixed components and then relate these to the molecular system. Thus if we use a notation where subscripts p and q refer to components respectively in space and molecular axis systems, the scalar product of $\underline{J}$ and $\underline{P}$ can be expanded as :

$$\begin{aligned} \underline{P}.\underline{J} &= \sum_p (-1)^p\, T^1_p(\underline{P})\, T^1_{-p}(\underline{J}) \\ &= \sum_{p,q} (-1)^p\, T^1_q(\underline{P}) \left[\mathcal{D}^1_{pq}(\omega)\right]^* T^1_{-p}(\underline{J}) \end{aligned} \tag{5.58}$$

Remembering that $\left[\mathcal{D}^1_{pq}(\omega)\right]^*$ does not commute with $T^1_{-p}(\underline{J})$, it might seem that the above expansion is not Hermitian, but luckily, on summing over p, all the non-commutation terms disappear. The matrix element of (5.58) is readily obtained by introducing the projection operator onto the complete manifold of rotational states (equals unity) between the rotation matrix and $T^1_{-p}(\underline{J})$. The matrix elements with $q\neq 0$ have the opposite sign to those given by reversed angular momentum methods. Thus the method of Freed [29], who mixed the two approaches, is not legitimate for the evaluation of matrix elements.

### 5.4.2 Rotational and Fine-structure Hamiltonian

The Hamiltonian appropriate to the ground vibronic state can be written in the form :

$$\begin{aligned} \mathcal{H}_{rso} &= B'(\underline{J}-\underline{L}-\underline{S})^2 + A'L_zS_z \\ &= B'\left\{\underline{J}^2+\underline{S}^2+L_z^2\right\} - 2B'T^1_0(\underline{J})T^1_0(\underline{L}) \\ &\quad - 2B'\underline{T}^1(\underline{J})\cdot\underline{T}^1(\underline{S}) + (A'+2B')T^1_0(\underline{L})T^1_0(\underline{S}) \end{aligned} \qquad (5.59)$$

where the term $B'(L_x^2+L_y^2)$, which affects all states equally, has been neglected. In a decoupled representation, its matrix elements may summarized as follows :

$$\langle \eta_0 \Lambda S \Sigma J \Omega M_J | \mathcal{H}_{rso} | \eta_0 S \Lambda \Sigma' J' \Omega' M_J \rangle$$

$$\begin{aligned}
&= \delta_{\Sigma\Sigma'}\,\delta_{\Omega\Omega'}\,B_0\left\{J(J+1) + S(S+1) + \Omega^2\right\} \\
&\quad - 2B_0\,\delta_{\Sigma\Sigma'}\,(-1)^{J-\Omega}\begin{pmatrix} J & 1 & J \\ -\Omega & 0 & \Omega' \end{pmatrix}\left\{J(J+1)(2J+1)\right\}^{\frac{1}{2}} \\
&\quad - 2B_0\sum_q (-1)^{J+S-\Omega-\Sigma}\begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega' \end{pmatrix}\begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \\
&\qquad\qquad \times \left\{S(S+1)(2S+1)J(J+1)(2J+1)\right\}^{\frac{1}{2}} \qquad (5.60) \\
&\quad + \delta_{\Sigma\Sigma'}\,(A_0 + 2B_0)\,(-1)^{S-\Sigma}\begin{pmatrix} S & 1 & S \\ -\Sigma & 0 & \Sigma' \end{pmatrix}\left\{S(S+1)(2S+1)\right\}^{\frac{1}{2}}
\end{aligned}$$

where $\langle\eta_0\Lambda|A'|\eta_0\Lambda\rangle$ and $\langle\eta_0\Lambda|B'|\eta_0\Lambda\rangle$ have been replaced by $A_0$ and $B_0$, the spin-orbit coupling constant and the rotational constant in the ground vibronic state. Since the matrix element is independent of nuclear spin and also of $M_J$, the same matrix elements are obtained in the coupled representation.

### 5.4.3 External Magnetic Field Interactions

The total effective Hamiltonian representing the interaction of the magnetic moments of the molecule with a magnetic field applied along the space-fixed z-axis is :

$$\begin{aligned}
\mathcal{H}_H &= \beta H\sum_q\left[\mathcal{D}^1_{0q}(\omega)\right]^*\left\{(g_L' + g_r')T^1_q(\underline{L}) + (g_s' + g_r + \Delta g_s(1-\delta_{q0}))\right. \\
&\qquad \left.\times\, T^1_q(\underline{S})\right\} - g_r T^1_0(\underline{J})H - \sum_\alpha g_\alpha\beta H\, T^1_0(\underline{I}_\alpha)
\end{aligned}$$

(5.61)

In the decoupled representation, the matrix elements are given by :

$$\langle \eta_0 \Lambda S \Sigma J \Omega M_J I M_I | \mathcal{H}_H | \eta_0 \Lambda S \Sigma' J' \Omega' M_J' I M_I' \rangle$$

$$= \beta H \sum_q (-1)^{\Omega - M_J} \left\{(2J+1)(2J'+1)\right\}^{\frac{1}{2}} \begin{pmatrix} J & 1 & J' \\ -M_J & 0 & M_J' \end{pmatrix}$$

$$\times \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \Big[ (g_L' + g_r)\Lambda + (g_s' + g_r + g_s(1-\delta_{q0}))$$

$$\times (-1)^{S-\Sigma} \left\{S(S+1)(2S+1)\right\}^{\frac{1}{2}} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \Big]$$

$$-(g_r \beta H M_J + \sum_\alpha g_\alpha \beta_N H M_I)\, \delta_{\Sigma\Sigma'} \delta_{JJ'} \delta_{M_J M_J'} \delta_{M_I M_I'} \qquad (5.62)$$

Using the coupled representation, the matrix elements become :

$$\langle \eta_0 \Lambda S \Sigma I J \Omega F M_F | \mathcal{H}_H | \eta_0 \Lambda S \Sigma' I J' \Omega' F' M_F \rangle$$

$$= \beta H \sum_q (-1)^{I+J'+2F-M_F+1} \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix}$$

$$\times \left\{(2F+1)(2F'+1)\right\}^{\frac{1}{2}} \Big[ (-1)^{J-\Omega} (g_L' + g_r)\Lambda \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \delta_{\Sigma\Sigma'}$$

$$\times \left\{(2J+1)(2J'+1)\right\}^{\frac{1}{2}} + (-1)^{J+S-\Omega-\Sigma} (g_s' + g_r + \Delta g_s(1-\delta_{q0}))$$

$$\times \left\{S(S+1)(2S+1)(2J+1)(2J'+1)\right\}^{\frac{1}{2}} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix}$$

$$+ g_r \left\{J(J+1)(2J+1)\right\}^{\frac{1}{2}} \delta_{\Omega\Omega'} \Big]$$

$$+ \quad g_{\alpha}\beta_{N}H\,(-1)^{I+J+F'+F-M_F}\left\{I(I+1)(2I+1)(2F+1)(2F'+1)\right\}^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} I & F & J \\ F' & I & 1 \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix} \delta_{JJ'}\,\delta_{\Omega\Omega'}\,\delta_{\Sigma\Sigma'} \qquad (5.63)$$

## 5.4.4 Magnetic Hyperfine Interactions

The magnetic interaction between the nuclear spin and an unpaired electron can be expressed as the sum of three terms representing the electron orbital-nuclear spin dipolar interaction, the Fermi contact interaction and the electron spin-nuclear spin dipolar interaction. This can be written in terms of spherical tensor operators as :

$$\mathcal{H}_1 = \sum_{i,\alpha} \frac{1}{r_{i\alpha}^{3}}\, 2\beta\, g_{\alpha}\, \beta_N \sum_{p,q} (-1)^{p} T^{1}_{-p}(\underline{I}_{\alpha}) \left[\mathcal{D}^{1}_{pq}(\omega)\right]^{*} T^{1}_{q}(\underline{l}_i') \qquad (5.64)$$

where $\underline{l}_i'$ is closely related to the orbital angular momentum $\underline{l}_i$ and has an identical molecular z component (see (3.210) ).

$$\mathcal{H}_2 = \sum_{i,\alpha} \frac{8\pi}{3}\, g\beta\, g_{\alpha}\, \beta_N\, \delta(r_{i\alpha}) \sum_{p,q} (-1)^{p} T^{1}_{-p}(\underline{I}_{\alpha}) \left[\mathcal{D}^{1}_{pq}(\omega)\right]^{*} T^{1}_{q}(\underline{s}_i) \qquad (5.65)$$

$$\mathcal{H}_3 = \sum_{i,\alpha} (30)^{\frac{1}{2}} g\beta\, g_{\alpha}\, \beta_N \sum_{p,q} (-1)^{p} T^{1}_{-p}(\underline{I}_{\alpha}) \left[\mathcal{D}^{1}_{pq}(\omega)\right]^{*} T^{1}_{q}(\underline{s}_i, \underline{C}^{2})$$

where $T^{1}_{q}(\underline{s}_i, \underline{C}^{2}) \; = \; \sum_{q_1 q_2} (-1)^{q} T^{1}_{q_1}(\underline{s}_i)\; C^{2}_{q_2}(\theta_i \phi_i) \begin{pmatrix} 1 & 2 & 1 \\ q_1 & q_2 & q \end{pmatrix} r_{i\alpha}^{-3}$

$$(5.66)$$

$C^k_q(\theta\phi)$ is related to the spherical harmonic $Y_{kq}(\theta\phi)$ by :

$$C^k_q(\theta\phi) = \left[\frac{4\pi}{2k+1}\right]^{\frac{1}{2}} Y_{kq}(\theta\phi) \qquad (5.67)$$

In the decoupled representation, the matrix elements are given by :

$$\langle \eta_0 \Lambda S \Sigma J \Omega M_J I M_I | \mathcal{H}_{hyp} | \eta_0 \Lambda S \Sigma' J' \Omega' M_J' I M_I' \rangle$$

$$= \sum_i \sum_{p,q} (-1)^{p+I+\Omega-M_I-M_J} \left\{I(I+1)(2I+1)(2J+1)(2J'+1)\right\}^{\frac{1}{2}}$$

$$\times \begin{pmatrix} I & 1 & I \\ -M_I & -p & M_I' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -M_J & p & M_J' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \beta g_\alpha \beta_N$$

$$\times \quad 2\delta_{\Sigma\Sigma'}\delta_{\Omega\Omega'} \langle \eta_0 \Lambda | r_i^{-3}\, T^1_0(\underline{l}_i) | \eta_0 \Lambda \rangle + (-1)^{S-\Sigma} \frac{8\pi}{3} g$$

$$\times \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \langle S \| T^1(\underline{s}_i) \| S \rangle \langle \eta_0 \Lambda | \delta(r_{i\alpha}) | \eta_0 \Lambda \rangle$$

$$+ (30/4)^{\frac{1}{2}} g \; (-1)^{q+S-\Sigma} \begin{pmatrix} 1 & 2 & 1 \\ q & 0 & -q \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix}$$

$$\times \langle S \| T^1(\underline{s}_i) \| S \rangle \langle \eta_0 \Lambda | \frac{3\cos^2\theta - 1}{r^3_{i\alpha}} | \eta_0 \Lambda \rangle \qquad (5.68)$$

The corresponding matrix elements in the coupled representation are :

$$\langle \eta_0 \Lambda S \Sigma I J \Omega F M_F | \mathcal{H}_{hyp} | \eta_0 \Lambda S \Sigma' I J' \Omega' F M_F \rangle$$

$$= \sum_q (-1)^{I+2J+F-\Omega} \beta g_\alpha \beta_N \left\{I(I+1)(2I+1)(2J+1)(2J'+1)\right\}^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} F & J & I \\ 1 & I & J' \end{Bmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix}$$

$$\times \Big[ 2 \langle \eta_0 \Lambda | r_i^{-3} \, T_0^1(\underline{l}_i) | \eta_0 \Lambda \rangle \delta_{\Sigma\Sigma'} \delta_{\Omega\Omega'} + (-1)^{S-\Sigma} \frac{8\pi}{3} g$$

$$\times \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \langle S \| T^1(\underline{s}_i) \| S \rangle \langle \eta_0 \Lambda | \delta(r_{i\alpha}) | \eta_0 \Lambda \rangle$$

$$+ (30/4)^{\frac{1}{2}} g \, (-1)^{q+S-\Sigma} \begin{pmatrix} 1 & 2 & 1 \\ q & 0 & -q \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix}$$

$$\times \langle S \| T^1(\underline{s}_i) \| S \rangle \langle \eta_0 \Lambda | \frac{3\cos^2\theta - 1}{r_{i\alpha}^3} | \eta_0 \Lambda \rangle \qquad (5.69)$$

where $C_0^2(\theta\phi)$ has been written explicitly as $\frac{1}{2}(3\cos^2\theta - 1)$. Also we have only considered one nuclear spin present in the molecule. The matrix element $\langle \eta_0 \Lambda | \delta(r_{i\alpha}) | \eta_0 \Lambda \rangle$ is the electron density of electron i at nucleus $\alpha$.

In the approximation that the electronic wave-function can be written as a single configuration with all paired electrons in identical orbitals, the summation over i need only be over unpaired electrons. In the case of a single unpaired electron $\underline{T}^1(\underline{s}_i)$ is replaced by $\underline{T}^1(\underline{S})$, with the consequence that $\langle S \| T^1(\underline{s}_i) \| S \rangle$ can be replaced by $\left\{ S(S+1)(2S+1) \right\}^{\frac{1}{2}}$. Analogously, the matrix element $\langle \eta_0 \Lambda | r_{i\alpha}^{-3} \, T_0^1(\underline{l}_i) | \eta_0 \Lambda \rangle$ can be replaced by $\Lambda \langle r_{i\alpha}^{-3} \rangle_L$ where $\langle \; \rangle$ means the expectation value.

Lucas [25], following the method of McWeeny [30], has used reduced density matrices to show that the term we have replaced by $\langle r_{i\alpha}^{-3} \rangle_L$ and often used as a parameter is not equal to the corresponding term in the spin-spin dipolar interaction. This is often implied in the statement that the expectation of $r_{i\alpha}^{-3}$ is different for spin and orbital angular momentum. They are only expected to be the same when the single configuration approximation is very good.

### 5.4.5 Electric Quadrupole Interaction

The electric quadrupole term represents the interaction of the nuclear electric quadrupole with the field gradient due to an external distribution of electrons. If we treat the nucleus classically as a number of point charges $Z_\beta$ at $\underline{r}_\beta$ with respect to the centre of mass, the Coulomb interaction $-Z_\beta e^2( \underline{r}_i - \underline{r}_\beta )^{-1}$ may be expanded as a power series in $r_\beta / r_i$. Then the multipole expansion [31] in terms of spherical harmonics yields :

$$\frac{1}{\underline{r}_i - \underline{r}_\beta} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2k+1} \frac{r_\beta^{l}}{r_i^{l+1}} Y_{l-m}(\theta_i \phi_i)\, Y_{lm}(\theta_\beta \phi_\beta) \qquad (5.70)$$

where $(r\theta\phi)$ are the spherical polar coordinates of a particle. The $l=0$ term has already been considered in the normal Coulomb interaction. The $l=1$ terms disappear since the nucleus has no electric dipole moment. It is the $l=2$ term that will be considered here (higher order terms are negligible); they give the quadrupole interaction.

Making the substitution :

$$T^2_m(\underline{Q}) = \sum_\beta Z_\beta r^2_\beta \; C^2_m(\theta_\beta \phi_\beta) \tag{5.71}$$

and

$$T^2_m(\underline{VE}) = \sum_i -\frac{1}{r_i^3} \, C^2_m(\theta_i \phi_i) \; , \tag{5.72}$$

the quadrupole Hamiltonian becomes :

$$\mathcal{H}_Q = e^2 \sum_{p,q} (-1)^p T^2_{-p}(\underline{Q}) \left[\mathcal{D}^2_{pq}(\omega)\right]^* T^2_q(\underline{VE}) \tag{5.73}$$

If the quadrupole moment of the nucleus is defined by [32] :

$$Q = 2 \left\langle II \,\middle|\, T^2_0(\underline{Q}) \,\middle|\, II \right\rangle \tag{5.74}$$

the matrix elements in the decoupled representation become :

$$\left\langle \eta_0 \Lambda S \Sigma J \Omega M_J I M_I \right| \mathcal{H}_Q \left| \eta_0 \Lambda S \Sigma J' \Omega' M_J' I M_I' \right\rangle$$

$$= \frac{e^2 Q}{2} \sum_{p,q} (-1)^{p+I-M_I+M_J-\Omega} \left\{(2J+1)(2J'+1)\right\}^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 2 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} J & 2 & J' \\ -M_J & p & M_J' \end{pmatrix} \begin{pmatrix} I & 2 & I \\ -M_I & -p & M_I' \end{pmatrix}$$

$$\times \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}^{-1} \left\langle \eta_0 \Lambda \right| T^2_q(\underline{VE}) \left| \eta_0 \Lambda' \right\rangle \tag{5.75}$$

In the coupled representation, the corresponding results are :

$$\langle \eta_0 \Lambda S \Sigma I J \Omega F M_F | \mathcal{H}_Q | \eta_0 \Lambda S \Sigma I J' \Omega' F M_F \rangle$$

$$= \frac{e^2 Q}{2} \sum_q (-1)^{I+F+2J-\Omega} \left\{(2J+1)(2J'+1)\right\}^{\frac{1}{2}} \begin{Bmatrix} F & J & I \\ 2 & I & J' \end{Bmatrix}$$

$$\times \begin{pmatrix} J & 2 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}^{-1} \langle \eta_0 \Lambda | T^2_q(\underline{\nabla E}) | \eta_0 \Lambda' \rangle \tag{5.76}$$

The $q=\pm 2$ component of the quadrupole interaction can contribute to the $\Lambda$-doubling, but as before this will be neglected. The matrix element of $2T^2_0(\underline{\nabla E})$ in the above equations is conventially written as $q_0$, the axial component of the electric field gradient. The quantity $e^2 q_0 Q$ which then results is called the quadrupole coupling constant.

### 5.4.6 Electric Field (Stark) Interaction

The Hamiltonian for a molecule in a uniform electric field, $\underline{E}$, can be obtained from (3.214) by replacing $\phi_\lambda$ by $-\underline{E}.(\underline{R} + \underline{r}_\lambda + \underline{\delta})$. Then for a non-charged molecule :

$$\mathcal{H}_E = -\underline{\mu}.\underline{E} \tag{5.77}$$

where $\underline{\mu} = \sum_\alpha e Z_\alpha \underline{r}_\alpha - \sum_i e \underline{r}_i$ is the dipole moment operator. In terms of spherical tensor operators, this becomes :

$$\mathcal{H}_E = -\sum_{p,q} (-1)^p T^1_p(\underline{E}) \left[\mathcal{D}^1_{-pq}(\omega)\right]^* T^1_q(\underline{\mu}) \tag{5.78}$$

Its matrix elements in the decoupled representation are :

$$\langle \eta_0 \Lambda S \Sigma J \Omega M_J | \mathcal{H}_E | \eta_0 \Lambda S \Sigma' J' \Omega' M_J' \rangle$$

$$= - \mu_0 \sum_p (-1)^{\Omega - M_J + p} \left\{ (2J+1)(2J'+1) \right\}^{\frac{1}{2}} \begin{pmatrix} J & 1 & J' \\ -M_J & -p & M_J' \end{pmatrix}$$

$$\times \begin{pmatrix} J & 1 & J' \\ -\Omega & 0 & \Omega' \end{pmatrix} T_p^1(\underline{E}) \, \delta_{\Sigma\Sigma'} \qquad (5.79)$$

In the coupled representation, the matrix elements are given by :

$$\langle \eta_0 \Lambda S \Sigma I J \Omega F M_F | \mathcal{H}_E | \eta_0 \Lambda S \Sigma' I J' \Omega' F' M_F' \rangle$$

$$= \mu_0 \sum_p (-1)^{I+J'+2F-M_F+J-\Omega+p} \left\{ (2F+1)(2F'+1)(2J+1)(2J'+1) \right\}^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ -M_F & -p & M_F' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & 0 & \Omega' \end{pmatrix} T_p^1(\underline{E}) \, \delta_{\Sigma\Sigma'} \qquad (5.80)$$

where $\mu_0$ is the dipole moment of the ground vibronic state.

### 5.4.7 Spin-rotation Interaction

The spin-rotation Hamiltonian is :

$$\mathcal{H}_{SR} = \gamma' \sum_{\substack{q=\pm 1 \\ p}} (-1)^q T_q^1(\underline{S}) \, \mathcal{D}_{p-q}^1(\omega) \, T_p^1(\underline{J}) \, , \qquad (5.81)$$

where certain constant terms, which affect all levels equally, have been omitted. In the decoupled representation, its matrix elements are given by :

$$\langle \eta_0 \Lambda S \Sigma J \Omega M_J | \mathcal{H}_{SR} | \eta_0 \Lambda S \Sigma' J \Omega' M_J \rangle$$

$$= \gamma' \sum_{q=\pm 1} (-1)^{J+S-\Omega-\Sigma} \left\{ S(S+1)(2S+1)J(J+1)(2J+1) \right\}^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \qquad (5.82)$$

Exactly the same results are obtained in the coupled representation.

The matrix elements of the electron spin-spin interaction will not be given here since in doublet states they are all identically zero.

## References to Chapter 5

1. M. Born and J. R. Oppenheimer, Ann. Physik. 84, 457 (1927).
2. M. Born and K. Huang, "Dynamical Theory of Crystal Lattices", (Oxford University Press, London, 1954), pp 166, 402, 406.
3. G. Herzberg, "Molecular Spectra and Molecular Structure. 1. Spectra of Diatomic Molecules", pp 219-226, (D. Van Nostrand, Princeton, N.J., 1950).
4. H. C. Longuet-Higgins, Advances in Spec. 2, 429 (1961).
5. Y.-N. Chiu, J. Chem Phys. 41, 3235 (1964).
6. D. M. Brink and G. R. Satchler, "Angular Momentum", (Oxford University Press, London, 1968).
7. M. E. Rose, "Elementary Theory of Angular Momentum", (John Wiley & Sons, New York, 1957).
8. M. Tinkham and M. W. P. Strandberg, Phys. Rev. 97, 937 (1955).
9. B. Rosenblum, A. H. Nethercot and C. H. Townes, Phys. Rev. 109, 400 (1958).
10. J. H. Van Vleck, Phys. Rev. 33, 467 (1929).
11. K. Kayama and J. C. Baird, J. Chem. Phys. 46, 2604 (1967).
12. P. R. Fontana and W. J. Meath, J. Math. Phys.
13. C. Bloch, Nuc. Phys. 6, 329 (1958).
14. A. Messiah, "Quantum Mechanics", Vol. 2, (North-Holland Publishing Co. Amsterdam, 1965).

16. T. A. Miller, Mol. Phys. 16, 105 (1969).

17. T. A. Miller, Ph. D. Thesis, (Cambridge, 1968).

18. A. Carrington, G. N. Currie, D. H. Levy and T. A. Miller, J. Chem. Phys. 50, 2726 (1969).

19. E. Hill and J. H. Van Vleck, Phys. Rev. 32, 250 (1928).

20. R. N. Dixon and H. W. Kroto, Trans. Far. Soc. 59, 1484 (1963).

21. J. T. Hougan, J. Chem. Phys. 36, 529 (1962).

22. L.-Y. C. Chiu, J. Chem. Phys. 40, 2276 (1964).

23. J. T. Hougan and I. Kopp, Can. J. Phys. 45, 2581 (1967).

24. G. N. Currie, Ph.D. Thesis, (Cambridge, 1968).

25. N. J. D. Lucas, Ph.D. Thesis, (Southampton, 1969).

26. E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra", (Cambridge University Press, London, 1935).

27. A. R. Edmonds, "Angular Momentum in Quantum Mechanics", (Princeton University Press, 1957).

28. J. H. Van Vleck, Rev. Mod. Phys. 23, 213 (1951).

29. K. F. Freed, J. Chem. Phys. 45, 4214 (1966).

30. R. McWeeny, J. Chem. Phys. 42, 1717 (1965).

31. M. E. Rose, "Multipole Fields", (Oxford University Press, 1955).

32. Y.-N. Chiu, J. Chem. Phys. 45, 2990 (1966).

# Chapter 6

# The E.p.r. Spectrum of the NS Radical

## 6.1 Introduction

The NS radical was first identified in mixtures of sulphur vapour and nitrogen, subjected to a discharge, by Fowler and Bakker [1]. Analysis of the $A^2\Sigma - X^2\Pi$ bands of the electronic spectrum by Zeeman [2] has given accurate values of the rotational constant ($B_0$) and the fine-structure constant (A) in the $^2\Pi$ ground state ($B_0=0.7705_8$ cm$^{-1}$, $A=223.0_3$ cm$^{-1}$)

The gas phase electron paramagnetic resonance spectrum of NS was first observed by reacting nitrogen atoms with hydrogen sulphide [3,4], but the signals were rather weak and broad. Subsequent studies [5] have shown that the reaction of nitrogen atoms with sulphur monochloride ($S_2Cl_2$) yields the spectrum with a signal-to-noise ratio of approximately 100 to 1. This permits accurate determinations of the axial component h of the hyperfine constant for the $^{14}N$ nucleus and the electric quadrupole coupling constant. The results also show a disagreement with Zeeman's value of $B_0$.

After the publication of these results [5], Uehara and Morino [6] observed the NS e.p.r. spectrum by discharging $N_2$ and $SCl_2$ together; their results are largely in agreement with those given here.

## 6.2 Experimental

The nitrogen atoms were obtained by passing 'oxygen-free' nitrogen, at a pressure of two torr, through a microwave discharge operated at 2450 MHz and at a power output of 100 watts; it was situated about 15 cm upstream of the Stark microwave cavity. The $S_2Cl_2$ vapour (previously de-gassed at liquid nitrogen temperatures) enters the cavity by a seperate inlet port, its flow being controlled by means of a needle valve.

The spectrum was observed using 100kHz Stark modulation. Ten series of measurements were made on the field position of each line; because of a small frequency drift, due to deposition of solid products in the cavity, all line positions were corrected to a constant frequency. Also, because of the slight perturbing effects of the cavity, the field inside the cavity differs slightly from that measured just outside. A correction of 2.7 gauss was thus made using NO as a standard [7]. The resulting fields are given in table 1, and the quoted errors of 0.2 gauss are twice the 'random' standard deviation. The remaining systematic error is probably less than 0.5 gauss.

In order to measure the dipole moment of NS, a static electric field of between 50 and 200 volts/cm was applied across the end-plates of the cavity. The full details are discussed in section (6.4).

## 6.3 Analysis of the Spectrum

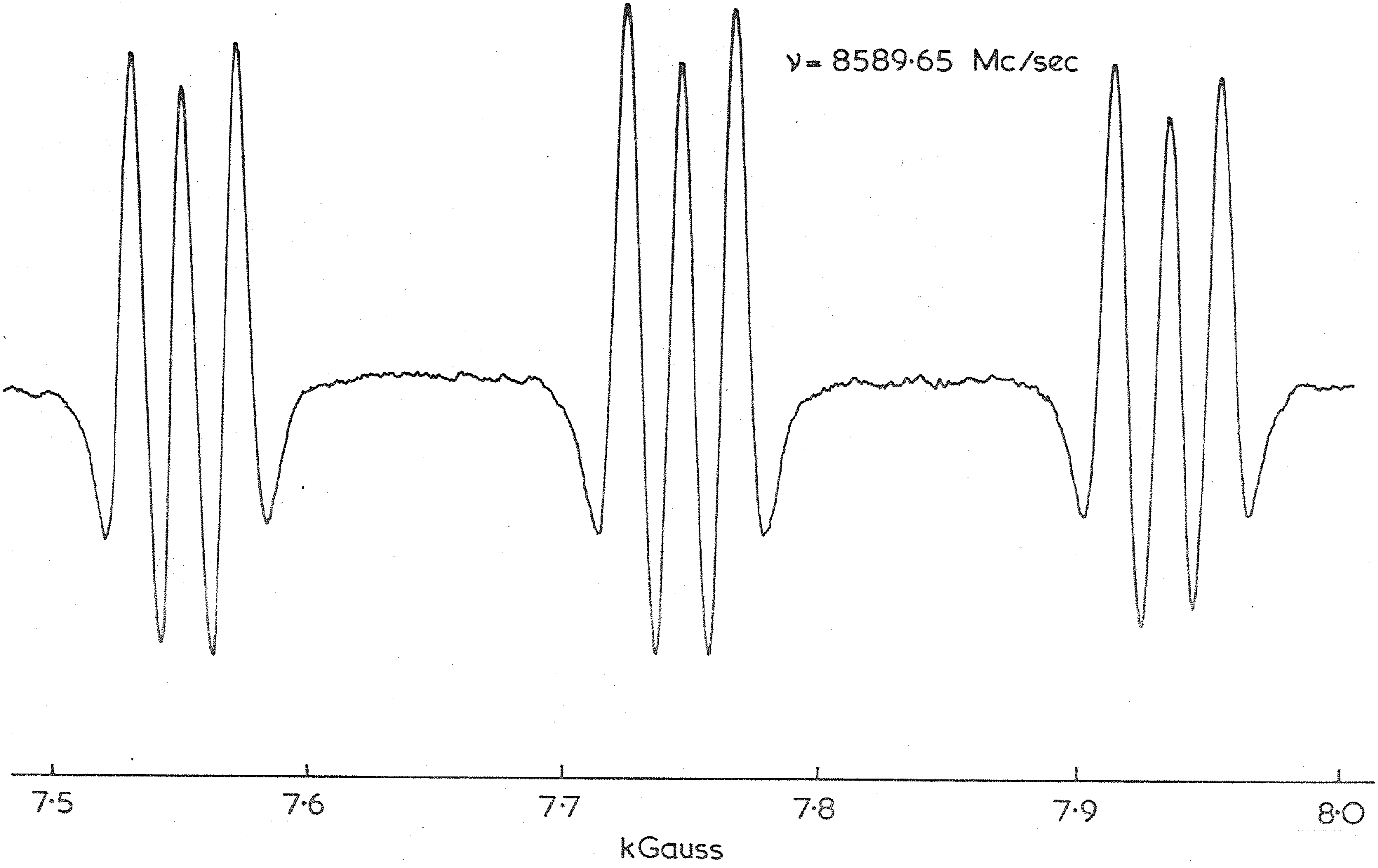
The electron resonance spectrum of NS, given in figure 1, consists of three triplets of lines. The centre of the spectrum indicates a g-value close to 0.8, the value expected for a good case (a) molecule in a $^2\Pi_{3/2}$ electronic state in its lowest rotational level ($J=3/2$). The basic spectrum corresponds to the three $\Delta M_J=\pm1$ transitions, further split into three by the $I=1$ $^{14}N$ magnetic nucleus.

The initial interpretation of the spectrum was made by means of a perturbation expansion for the energy levels. Then, using the fact that the electron resonance transitions quite accurately obey the selection rules $\Delta M_J=\pm1, \Delta M_I=0$ in a decoupled representation, the resonant frequency for each line can be written as a power series in the magnetic field, H, with coefficients expressed in terms of the molecular parameters A, $B_0$, h and $e^2Qq_0$. Since high order terms are required, the expansion is best performed using projection operators. This technique can cope with degeneracies but here it is convenient to remove the degeneracy of states with the same value of J but different $M_J$ by defining a suitable zeroth order Hamiltonian. Thus the total Hamiltonian can be written as :

$$\mathcal{H} = \mathcal{H}_0 + V + V' \qquad (6.1)$$

where,

$$\mathcal{H} = \mathcal{H}_{rso} + \frac{\beta H(\Lambda + g\Sigma)\Omega}{J(J+1)} M_J \qquad (6.2)$$



<u>Figure 6.1</u> Gas phase e.p.r. spectrum of NS in its J = 3/2 level.

$\mathcal{H}_o$ removes the degeneracy of states with different values of J, $M_J$ or $\Omega$. Then the main perturbation term, V, is :

$$V = \beta \underline{H}.(\underline{L} + g\underline{S}) - \frac{\beta H(\Lambda + g\Sigma)\Omega}{J(J+1)} M_J \qquad (6.3)$$

V' contains all the relatively small terms :

$$V' = \mathcal{H}_{hyp} + \mathcal{H}_Q + g_r \beta \underline{H}.(\underline{J}-\underline{L}-\underline{S}) - g_N \beta_N \underline{H}.\underline{I}$$

$$+ \beta \underline{H}.(\delta g_L \underline{L} + \delta g_S \underline{S}) \qquad (6.4)$$

where $\delta g_L$ and $\delta g_S$ are small mass-polarization and relativistic corrections to the orbital and spin g-factors.

Then using degenerate perturbation theory [8,9,10], the energy of a particular state, $|0\rangle$, is given to fourth order by :

$$E = \langle 0|P_o \mathcal{H}\mathcal{U}|0\rangle = \langle 0|\mathcal{H}_o|0\rangle + \langle 0|V|0\rangle + \langle 0|V'|0\rangle$$

$$+ \langle 0|V(Q_o/a)V(Q_o/a)V|0\rangle + \langle 0|V(Q_o/a)V|0\rangle$$

$$+ \langle 0|V(Q_o/a)V(Q_o/a)V(Q_o/a)V|0\rangle + \langle 0|V(Q_o/a^2)VP_oV(Q_o/a)V|0\rangle$$

$$+ \langle 0|V(Q_o/a)V(Q_o/a)V(Q_o/a)V(Q_o/a)V|0\rangle$$

$$- \langle 0|V(Q_o/a^2)V(Q_o/a)VP_oV(Q_o/a)V|0\rangle$$

$$- \langle 0|V(Q_o/a^2)V\ P_oV(Q_o/a)V(Q_o/a)V|0\rangle$$

$$- \langle 0|V(Q_o/a)V(Q_o/a^2)V\ P_oV(Q_o/a)V|0\rangle \qquad (6.5)$$

where $P_o$ is the projection operator onto the particular eigenstate $|0\rangle$ of $\mathcal{H}_o$ and $Q_o$ projects onto all the other states $|n\rangle$ such that :

$$\frac{Q_o}{a^r} = \sum_{n\neq 0} \frac{|n\rangle\langle n|}{(E_o-E_n)^r} \qquad (6.6)$$

This type of expansion has been given previously by Freed [10], but the one given here differs in the fact that the perturbation V has zero diagonal matrix elements in the ground state, i.e. $P_oV\,P_o$ is zero. After evaluating the matrix elements in (6.5) the energy of each state can be obtained as a power series in H. Then neglecting for the moment the hyperfine interactions and other small terms, V', the transition energies of the transitions $(M_J \leftrightarrow M_J+1)$ are as given below; we shall make use of the abreviation : $k = (1+g/2)\beta H$ and $l = g\beta H$ $(g=2.002319)$.

$$\begin{aligned} E(\pm\tfrac{3}{2}\leftrightarrow\pm\tfrac{1}{2}) &= 0.40000k \pm 0.05333\left(\frac{k}{5B}\right)k - 0.01829\left(\frac{k}{5B}\right)^2k \\ &\mp 0.0186\left(\frac{k}{5B}\right)^3k - \frac{0.800\ Bl}{A-2B} \\ &\mp \frac{0.1667\ l^2}{A+B} \pm \frac{0.1067\ l^2}{A-2B} - \frac{0.0067\ l^2}{A-7B} \\ &+ \text{ small (higher order) terms ,} \qquad (6.7) \end{aligned}$$

$$\begin{aligned} E(+\tfrac{1}{2}\leftrightarrow-\tfrac{1}{2}) &= 0.40000k - 0.03657\left(\frac{k}{5B}\right)^2k - \frac{0.8000\ Bl}{A-2B} \\ &+ \text{ higher order terms} \qquad (6.8) \end{aligned}$$

In equation (6.7), all upper signs and all lower signs are to be taken together.

The principal term for all lines is 0.4k, yielding a g-value of 0.8. The main contribution to the seperation of the different $\Delta M_J=\pm1$ transitions is the second order Zeeman term, $0.0533k^2/5B$. This is inversely proportional to B and allows a determination of the rotational constant. After allowing for certain contributions from the third order Zeeman effect, the main term which affects the position of the centre of the spectrum is $-0.8Bl/(A-2B)$ ; hence the fine-structure constant A can readily be determined. There is a further contribution to the overall g-value from V', namely $0.4g_r+0.4(\delta g_L+\frac{1}{2}\delta g_S)$. These are all typically of the order of $10^{-4}$ and if neglected represent an uncertainty of A; see for example the ClO spectrum [11].

The first order contributions of the hyperfine interactions to the transition energies are :

$$E'(M_J\leftrightarrow M_J+1) = 0.4h\, M_I + 0.05\, e^2Qq_0(2M_J+1)\,\frac{\left\{3M_I^2-I(I+1)\right\}}{I(2I-1)} \tag{6.9}$$

Thus the seperation in the centre group of lines is essentially independent of $e^2Qq_0$ and gives the magnitude of the hyperfine constant, h, although not its sign (this can be often obtained from higher order effects). The outer groups of lines show some asymmetry due to the quadrupole interaction. For nuclear spin I=1, the $M_I=\pm1$ components are both moved by $0.1e^2Qq_o$ ($-0.1e^2q_0Q$) to higher frequency for $M_J=\frac{1}{2}$ ($M_J=-3/2$), and the $M_I=0$ centre component is moved by $0.2e^2q_0Q$ in the opposite direction. Thus the asymmetry in spacing of the outer two groups of lines gives $0.6e^2q_0Q$; its sign is obtained even though it may not be possible to identify which transition corresponds to $M_I= +1$ or $-1$.

The energy levels were calculated accurately by computer diagonalisation of the matrix representing the effective Hamiltonian in either a coupled or decoupled case (a) representation. Inclusion of the first four rotational levels in each fine-structure state was found to give negligible rounding off errors. Initially the values $A=223.0_3$, $B_0=0.7705_8$ cm$^{-1}$, given by Zeeman [2], were used together with the first order values of h and $e^2q_oQ$, obtained from the perturbation treatment. After slight modification of h and $e^2q_0Q$, the calculated line positions are given in table 1, column 2. The predicted line positions are on average about 0.7 gauss too low. As mentioned previously, agreement with experiment could be obtained by using an 'effective' A value (cf. ClO [11]). Instead the value of A obtained from the electronic spectrum was assumed to be correct. The remaining discrepancy in the absolute position can be removed by putting $(g_r+\delta g_L+\frac{1}{2}\delta g_s)$ equal to $-1.7\times10^{-4}$; the results are given in column 2 of table 1.

Table 6.1 : Comparison of the measured and calculated field positions for the e.p.r. spectrum of NS. The microwave frequency is 8589.650 MHz.

| $M_J$ | $M_I$ | Observed field | Calculated field (a) | Calculated field (b)* | Calculated field (c)** | Calculated field (d)** |
|---|---|---|---|---|---|---|
|  | 1 | 7533.42 | 7532.45 | 7533.09 | 7533.51 | 7533.57 |
| $3/2 \leftrightarrow 1/2$ | 0 | 7553.22 | 7552.17 | 7552.81 | 7553.23 | 7553.23 |
|  | -1 | 7574.50 | 7573.42 | 7574.06 | 7574.49 | 7574.42 |
|  | 1 | 7725.68 | 7725.04 | 7725.69 | 7725.70 | 7725.70 |
| $1/2 \leftrightarrow -1/2$ | 0 | 7746.09 | 7745.55 | 7746.20 | 7746.21 | 7746.21 |
|  | -1 | 7766.48 | 7765.88 | 7766.54 | 7766.55 | 7766.55 |
|  | 1 | 7912.18 | 7911.96 | 7912.62 | 7912.24 | 7912.17 |
| $-1/2 \leftrightarrow -3/2$ | 0 | 7933.56 | 7933.22 | 7933.88 | 7933.51 | 7933.51 |
|  | -1 | 7953.07 | 7952.67 | 7953.33 | 7952.95 | 7953.02 |

* Using $g_r + \delta g_L + \frac{1}{2}\delta g_S = -1.72\times10^{-4}$.

** Using $B_0 = 0.7722$ cm$^{-1}$ and the g-factor corrections given above.

The second order Zeeman splitting, as calculated by matrix diagonalisation, between the three $\Delta M_J=\pm1$ groups is about 0.4 gauss too small. This is significantly outside the experimental accuracy and suggests that the rotational constant, $B_o$, should be modified, although a close examination of Zeeman's analysis of the u.v. spectrum gives no strong reason for such a change. The magnetic susceptibility terms which have been neglected can affect the second order Zeeman splitting, but a calculation of the magnitude of such an effect confirms that it is negligible at 10 kgauss. The rotational constant was changed from 0.7706 to 0.7722 $cm^{-1}$ and its effect on the spectrum is given in table 1, column 4.

It has been assumed that the hyperfine constant is positive as in NO. The effect of reversing the sign of h is given in column 5 of table 1.

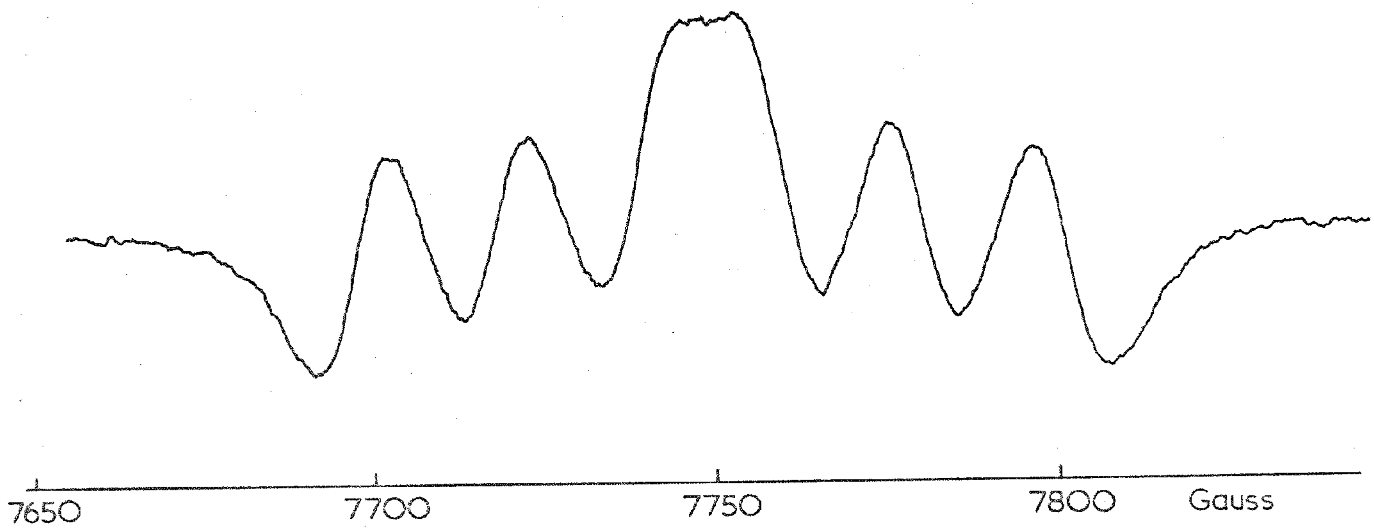
The perpendicular (non-axial) component, b, of the hyperfine interaction mixes the fine-structure states and slightly affects the hyperfine splitting. However since it has the same effect as a change in h, it is impossible to seperate the two contributions. Order of magnitude calculations suggest that the effect on the measured magnitude of h is about the same as the experimental error limits, so will not be important. The whole problem is considered in more detail in the next chapter on CF, where it is much more important.

Finally, one should consider the spin-rotation interaction, since the spin-rotation constant is typically of the order of 100 MHz. However, in a good case (a) molecule, the first order contribution is zero; this is because the spin and rotational magnetic moments are essentially perpendicular. Second order contributions are independent of $M_J$, so that for a given value of J all levels are moved by the same amount; the effect on the spectrum is thus nil. Higher order effects are completely negligible in a reasonably good case (a) molecules.

## 6.4 The Stark Effect and Dipole Moment of NS

In the presence of a strong electric field, each line of the NS spectrum is split into two component. The effect of a field of about 100 volt/cm is shown in figure 2. Measurement of the splitting as a function of applied electric field enables one to determine the dipole moment of the molecule.

The effective electric inside the microwave cavity was obtained by measuring the splitting in the NO spectrum before and after each run on NS and using the known value of its dipole moment [12]. Care has to be taken to prevent electrons from getting into the cavity and reducing the effective electric field seen by the NS radical. Initial results were somewhat low. The free electrons appear to be formed by photoionisation, which was minimised by placing a bend in



<u>Figure 6.2</u> Stark splitting of the centre group of NS at a field of 80 volts/cm.

the flow tube between the microwave discharge region and the cavity. It is believed that the dipole moments calculated now are accurate to the errors quoted because of the low number of free electrons present in the microwave cavity.

The Hamiltonian in the presence of a static electric field is given by :

$$\mathcal{H}' = \mathcal{H} + \mathcal{H}_E \qquad (6.10)$$

where

$$\mathcal{H}_E = -\underline{\mu}.\underline{E} \qquad (6.11)$$

In the absence of $\mathcal{H}_E$, the basis wave-functions may be written as

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left\{|\eta_o \Lambda S \Sigma J \Omega M_J I M_I\rangle + (-1)^{J-S}|\eta_o -\Lambda S -\Sigma J -\Omega M_J I M_I\rangle\right\} \qquad (6.12)$$

Although these states are not eigenfunctions of $\mathcal{H}$, it is possible by means of a suitable transformation (such as that given in section 6.3) to obtain an effective Hamiltonian diagonal in our basis. The two states given above have almost the same energy, being seperated by the $\Omega$-doubling constant. The electric field interaction does not preserve parity and mixes these two states. In an early paper on the Stark effect [13], only the first order contribution of $\mathcal{H}_E$ was considered but here third order contributions will be included. Then by means of degenerate perturbation theory, the off-diagonal elements in the matrix :

$$\begin{bmatrix} W + \delta/2 & S \\ S & W - \delta/2 \end{bmatrix} \qquad (6.13)$$

representing the mixing of the two $\Omega$-doublets are given by :

$$\begin{aligned} S \;=\; & \langle + | \mathcal{H}_E | - \rangle + \langle + | P_o \mathcal{H}_E (Q_o/a) V | P_o | - \rangle + \langle + | P_o \mathcal{H}_E (Q_o/a) V P_o | - \rangle \\ & + \langle + | \mathcal{H}_E (Q_o/a) V (Q_o/a) V | - \rangle + \langle + | V (Q_o/a) \mathcal{H}_E (Q_o/a) V | - \rangle \\ & + \langle + | V (Q_o/a) V (Q_o/a) \mathcal{H}_E | - \rangle - \langle + | V (Q_o/a^2) V P_o \mathcal{H}_E | - \rangle \\ & + \text{higher-order terms} , \qquad (6.14) \end{aligned}$$

where V is given in (6.3). Terms like $\langle + | \mathcal{H}_E (Q_o/a^2) V P_o V | - \rangle$ have been omitted because the diagonal matrix elements of V are zero.

The eigenvalues of the secular determinant from (6.13) are given by :

$$E = W \pm \tfrac{1}{2} ( \delta^2 + 4S^2 )^{\frac{1}{2}}, \qquad (6.15)$$

and since at the field strengths used in the experiment, $S \gg \delta$, the seperation of the $\Omega$-doublet components is given by :

$$\Delta E = 2S + \frac{\delta^2}{4S} + \text{higher order terms.} \qquad (6.16)$$

The first order variation of the intensities of the transitions has been considered previously. At high electric fields only some of the transitions have significant transition probability. Measurements were performed on the $M_J = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions and for any given $M_I$

the observed Stark splitting between the two strongly allowed transitions is give by :

$$\Delta\varepsilon = 0.8\mu E - 0.219\mu E(2\beta H/5B)^2 + 2.5\,\delta^2/E \quad (6.17)$$

Although $\delta$ must be included for NO with its small Stark splitting in the calibration of the electric field, it can be completely neglected for NS ($\mu E$ is typically of the order of 40 MHz while $\delta$ is less than 1 MHz). Then using the known values of the dipole moment (o.15872 Debye) [12] and the $\Omega$-doubling constant (0.91 MHz) [7] for NO, the mean of the calculated values of the electric dipole moment of NS is 1.86 ± 0.08 Debye.

## 5.5 Discussion of Results

The agreement between the theoretical analysis and experimental observations is good, apart from the small discrepancy in $B_0$. Since these measurements, the microwave spectrum of NS has been observed by Amano et al [14]. They affirm the discrepancy in Zeeman's value of $B_0$; their value of the rotational constant, $B_0 = 23156.0\ \text{MHz} = 0.7724\ \text{cm}^{-1}$, is in good agreement with the value obtained here. The microwave spectrum also gives information on the $\Omega$-doubling parameters and the various contributions to the hyperfine constants. They were not able to completely seperate off the perpendicular contribution which mixes the fine-structure states.

The results are compared with those of the present work in table 2. The single configuration approximation has been made by Uehara and Morino [6] to obtain a value of b = 64 MHz. The uncertainty in this (cf the discrepancy in the hyperfine constant c obtained by different methods in table 2) could be around 50% but this is not important here since its effect on the spectrum and hence the change in h is small. After this mobification it is found that h should be increased from 56.8 to 57.4 MHz.

The NS radical might be expected to have an electronic structure similar to that of NO, and the molecular parameters for the two are compared in table 2. The hyperfine parameters for NS are slightly smaller than in NO, suggesting that the unpaired electron is less localised on the nitrogen atom, although this semi-qualitative interpretation is somewhat unsatisfactory.

Since the dipole moments of NO and SO are 0.158 and 1.55 Debye respectively, simple electronegativity arguments indicate that our value of 1.86 Debye for NS is not unexpected (if they reinforce one another). The dipole moment of NO is so small that there must be some doubt about its sign, but in NS it seems reasonably certain that the negative end of the dipole is on the nitrogen. Just recently, a wave-function calculation has confirmed this with a value of 1.73 Debye for the dipole moment.[14]

Table 6.2 : Comparison of the molecular parameters of NS, obtained by different authors, and those of NO.

| Parameter | NS<br>This work | NS<br>E.p.r. ref 4 | NS<br>Microwave[13] | NO |
|---|---|---|---|---|
| A | $223.0_3$ cm$^{-1}$ | — | $222.9_4$ cm$^{-1}$ | 123.16 cm$^{-1}$ |
| $B_0$ | 0.7722 cm$^{-1}$<br>23150 ± 10 MHz | —<br>23161 MHz | —<br>23156.01 MHz | 1.6957 cm$^{-1}$ |
| $h = a + \frac{1}{2}(b+c)$ | 56.8 ± 0.5 MHz | 57.0 ± 0.2 MHz | | |
| After correction | 57.4 ± 0.5 MHz | 57.6 ± 0.2 MHz | $56.3_5$ ± 0.8 MHz | 75.8 ± 0.2 MHz |
| $a - \frac{1}{2}(b+c)$ | — | — | 67.4 ± 0.5 MHz | 92.7 ± 1.0 MHz |
| d MHz | — | — | 87.0 ± 0.4 | 112.60 |
| a MHz | — | — | 61.9 ± 0.7 | 84.28 ± 0.5 |
| (b+c) MHz | — | — | −11.1 ± 1.3 | −16.9 ± 1.0 |
| $c = 3(a-d)$ * | — | — | −75.4 MHz | −84.9 MHz |
| $d = -d/2$ ** | — | — | −43.5 MHz | −56.3 MHz |
| $e^2q_0Q$ MHz | −3.1 ± 0.5 | $-2.8_6$ ± 0.3 | −2.6 ± 0.7 | −1.8 |
| $\mu$ Debye | 1.86 ± 0.08 | — | 1.81 ± 0.5 | 0.15872 |

* Assuming a single configeration so that $\langle r^{-3}\rangle_L = \langle r^{-3}\rangle_S$

** Assuming that the wave-function near the $^{14}$N nucleus is like a p-orbital.

## References to Chapter 6

1. A. Fowler and C. Bakker, Proc. Roy. Soc. A136, 28 (1937)
2. P. B. Zeeman, Can. J. Phys. 29, 174 (1951)
3. A. Carrington, G. N. Currie, P. N. Dyer, D. H. Levy and T. A. Miller, Chem. Comm. 641 (1967).
4. J. C. Robertson, Ph. D. Thesis,(Cambridge, 1967).
5. A. Carrington, B. J. Howard, D. H. Levy and J. C. Robertson, Mol. Phys. 15, 187 (1968)
6. H. Uehara and Y. Morino, Mol. Phys. 17, 239 (1969).
7. R. L. Brown and H. E. Radford, Phys. Rev. 147, 6 (1966).
8. A. Messiah, "Quantum Mechanics" Chapter 14 (North-Holland Publishing Co., Amsterdam, 1965).
9. C. Bloch, Nuc. Phys. 6, 329 (1958).
10. K. F. Freed, J. Chem. Phys. 45, 4214 (1966).
11. A. Carrington, P. N. Dyer and D. H. Levy, J. Chem. Phys. 47, 1756 (1967)
12. W. Klemperer and R. M. Neumann, (Private communication, 1969).
13. A. Carrington, D. H. Levy and T. A. Miller, J. Chem. Phys. 47, 3801 (1967).
14. T. Amano, S. Saito, E. Hirota and Y. Morino, J. Mol. Spec. 32, 97 (1969).
15. P. A. G. O'Hare, J. Chem. Phys. 52, 2992 (1970).

# Chapter 7

## Gas-phase E.P.R. Spectrum of CF

### 7.1 Introduction

The free radical CF has been known for some 20 years. Its $A^2\Pi - X^2\Pi$ band system was first identified and analysed by Andrews and Barrow [1] who studied the flash photolysis of $CF_4$. More accurate values of the rotational constant $B_0$ and the spin-orbit coupling (fine structure) constant A in the ground vibronic state have recently been obtained by Porter et al. [2]; these values are confirmed by the work to be described here. The e.p.r. measurements are concerned with the $^2\Pi_{\frac{3}{2}}$ state which is about 77 $cm^{-1}$ above the essentially diamagnetic $^2\Pi_{\frac{1}{2}}$ ground-state.

From the observed hyperfine splitting in the spectrum, it is possible to obtain a value for the axial component (h) of the $^{19}F$ magnetic hyperfine interaction. In addition, the relatively small value of $A/B_0$ means that there is considerable rotational mixing of the two fine-structure states, with the consequence that the perpendicular component (b) of the hyperfine interaction has a significant effect upon the electron resonance spectrum. To first order in the hyperfine interaction this effect is the same as that of the axial component h and the measurements on CF in its lowest rotational level ($J=\frac{3}{2}$) provide a relationship between h and b, but do not enable their seperate values to be determined. In the second rotational level ($J=\frac{5}{2}$), however, the rotational mixing of the fine-structure states is greater, so that a second relationship between h and b is obtained. It is thus possible to seperate h and b. As we shall see, the various contributions to the hyperfine interaction, for example the Fermi-contact interaction, are still not uniquely determined but the use of a simple L.C.A.O. model of the electronic structure gives significant information.

Measurement of the splitting of each line by an applied electric field, which is essentially first order, has yielded the value of the electric dipole moment.

## 7.2 Experimental

The electron resonance spectrum of CF was obtained by passing $CF_4$ through a microwave discharge and mixing the discharge products with a secondary gas inside the resonant microwave cavity of the spectrometer. The secondary gas was any one of a number of organic molecules containing hydrogen atoms adjacent to an electron withdrawing group. The most successful were acetonitrile, acetone, acetaldehyde and ketene, of which the last two yielded the strongest CF spectra. Since, however, the reaction with acetaldehyde produced a polymeric deposit in the spectrometer cavity, ketene was used for most experiments. The preparation of ketene is described in section

(2.6). The electron resonance spectrum was observed in a Decca Stark cavity (similar to that designed by Carrington et al. [3]) with a Decca X-3 spectrometer used in conjunction with a Varian 15 in. magnet. The magnet field positions of the CF lines were measured by means of an A.E.G. fluxmeter.

Several series of measurements were made on each line and after correction to a constant microwave frequency, the mean was calculated. A small correction was made for the slight difference in magnetic field between the inside and outside of the cavity; the final results are given in Table 1. The standard error in the line positions for the J=3/2 level is 0.4 gauss.

In the J=5/2 level, however, the spectrum was very weak and therefore time-averaging techniques were used to improve the signal-to-noise ratio. At the highest fields used, the inhomogeneity close to the pole faces was too great for the proton resonance absorption to be observable; the field was therefore calibrated with the proton resonance probe in the centre of the magnet gap, the microwave cavity being removed. In this way it was possible to measure the hyperfine splittings to within ±1.5 gauss, but the absolute field values given in table 2 are only accurate to about ±7 gauss. Fortunately our main interest is in the J=5/2 hyperfine splittings, which are reasonably well determined.

The electron paramagnetic spectra of CF in its J=3/2 and

$J=5/2$ levels are shown in figures 1 and 2 respectively. Since the maximum magnetic field available is about 22 kilogauss, it is not possible to measure the two highest field doublets.

Dipole moment measurements were carried out carried out by applying static electric fields of up to 200 volts/cm across the microwave cavity; care was taken to minimise the number of free electrons present, formed by photoionisation. Each line in the $J=3/2$ spectrum is split into two out-of-phase first derivative components [4], and the splitting as a function of electric field strength yields the dipole moment. The electric field inside the cavity was calibrated by observing the Stark splitting in NO before and after each CF measurement; the dipole moment of NO is known accurately to be 0.15872 Debye [5].

## 7.3 Analysis of the Spectra

The electron resonance spectra were analysed by means of the effective Hamiltonian derived in section 5.3.

The spectrum of CF in the $J=3/2$ level consists of six lines, with a centre corresponding to a g-value close to 0.8, the value expected for a ${}^2\Pi_{3/2}$, $J=3/2$ state with good case (a) coupling. The six lines arise from the three electric dipole allowed $\Delta M_J=\pm1$ transitions, each split into two by the magnetic hyperfine coupling of the ${}^{19}$F nucleus, which has spin $I=\frac{1}{2}$; the hyperfine splitting in

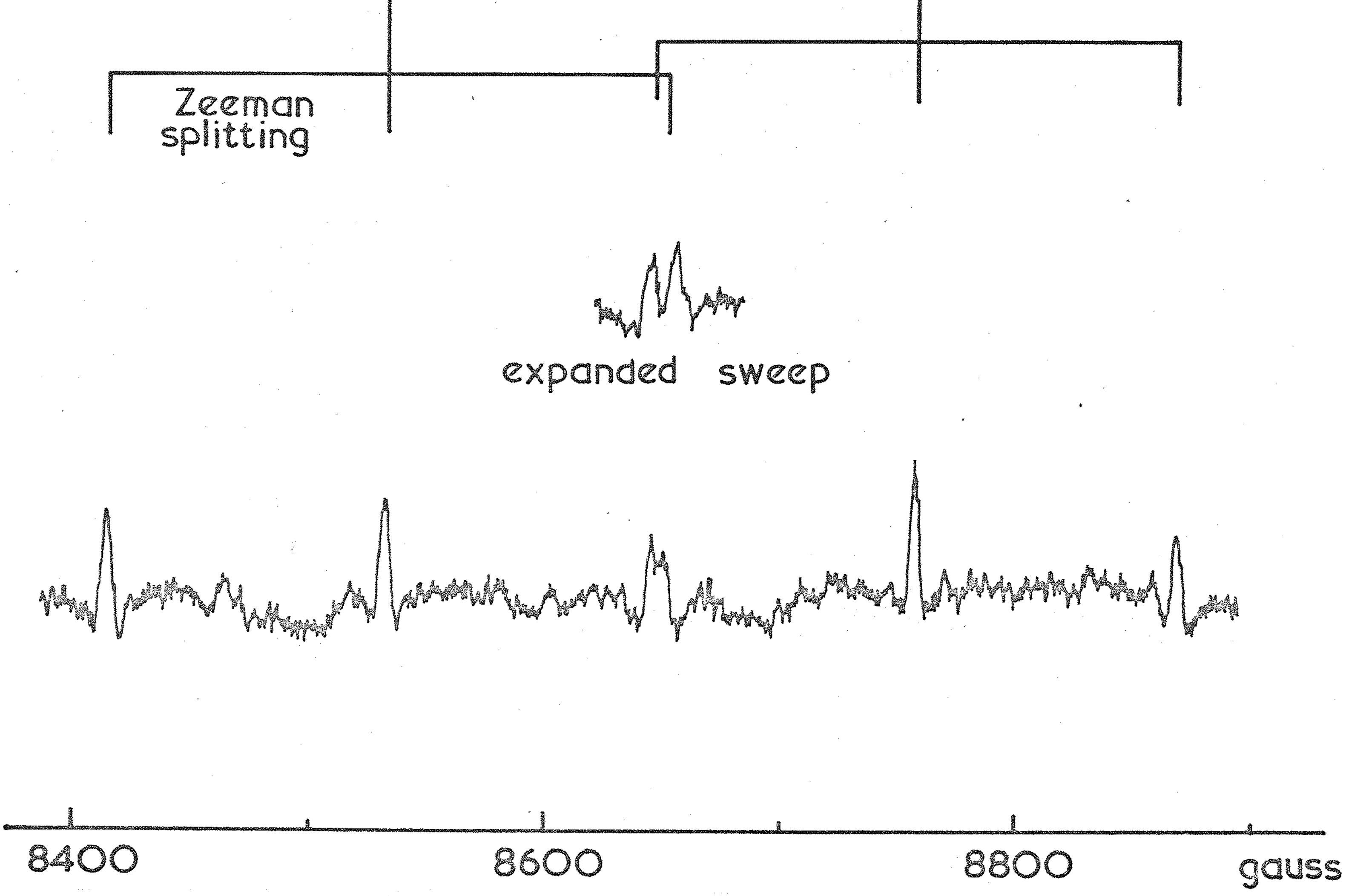


Figure 7.1 Gas phase e.p.r. spectrum of CF in its $J = 3/2$ level. The doublet splitting of the centre line is shown on an expanded field sweep.

Table 7.1 : The experimental and calculated field positions (in gauss) for the J=3/2 rotational level. The error in measured field positions is ±0.4 gauss.

The microwave frequency is 9270.22 MHz.

| $M_J$ | $M_I$ | Observed field | Calculated field (a) | Calculated field (b) |
|---|---|---|---|---|
| $-3/2 \leftrightarrow -1/2$ | $-\frac{1}{2}$ | 8859.8 | 8859.8 | 8859.8 |
| | $\frac{1}{2}$ | 8623.4 | 8623.1 | 8623.0 |
| $-1/2 \leftrightarrow 1/2$ | $-\frac{1}{2}$ | 8740.2 | 8740.0 | 8740.0 |
| | $\frac{1}{2}$ | 8496.8 | 8496.9 | 8496.8 |
| $1/2 \leftrightarrow 3/2$ | $-\frac{1}{2}$ | 8617.5 | 8617.9 | 8617.9 |
| | $\frac{1}{2}$ | 8367.6 | 8368.0 | 8368.1 |

(a) Using $h = 655.6$ MHz, $b = 0.0$ MHz, $g' = -0.00006$.

(b) Using $h = 662.9$ MHz, $b = 190$ MHz, $g' = -0.00006$.

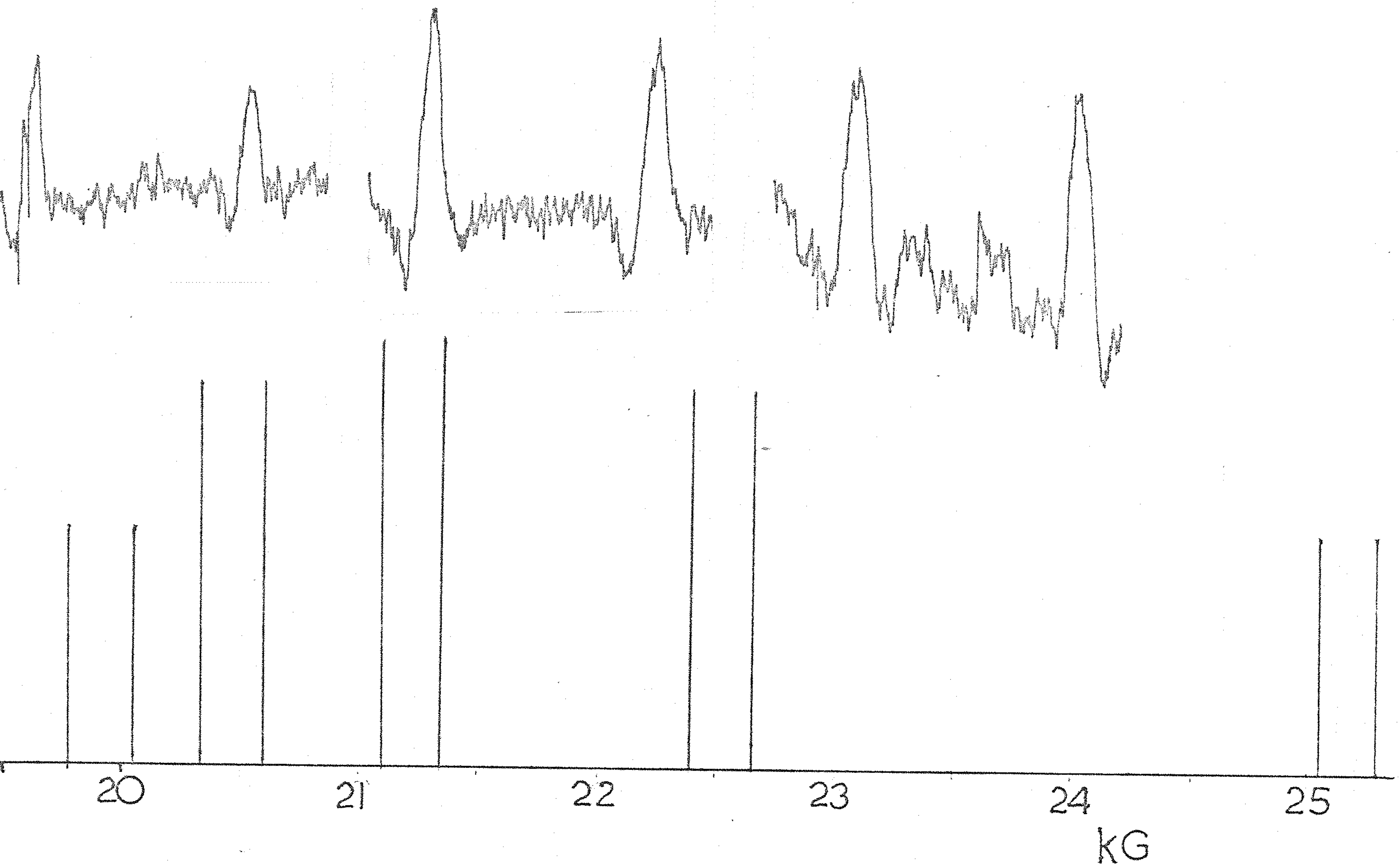


Figure 7.2 Gas phase e.p.r. spectrum of CF in its $J = 5/2$ level

Table 7.2 : The experimental and calculated field positions (in gauss) for the J=5/2 rotational level. The error in the experimental hyperfine splittings is ± 1.5 gauss, but the absolute field positions are only accurate to ± 7 gauss. The microwave frequency is 9270.2 MHz.

| $M_J$ | $M_I$ | Observed field | Observed hyperfine splitting | Calculated field * | Calculated hyperfine splitting |
|---|---|---|---|---|---|
| -1/2 1/2 | $-\frac{1}{2}$ | 21382.4 | 253.2 | 21376.9 | 253.8 |
| | $\frac{1}{2}$ | 21129.2 | | 21123.1 | |
| -3/2 -1/2 | $-\frac{1}{2}$ | 20581.8 | 251.2 | 20585.7 | 249.4 |
| | $\frac{1}{2}$ | 20330.6 | | 20336.3 | |
| -5/2 -3/2 | $-\frac{1}{2}$ | 20042.2 | 247.3 | 20043.8 | 248.6 |
| | $\frac{1}{2}$ | 19794.9 | | 19795.2 | |

* Using the final values of h and b, namely h = 662.9 MHz, b = 190 MHz. The overall g-value correction is g' = 0.0001.

the spectrum is approximately twice as large as the second-order Zeeman splitting of the $\Delta M_J=\pm 1$ transitions. An approximate calculation of the Zeeman splitting using perturbation theory gives a value of the rotational constant $B_0$ close to 1.40 $cm^{-1}$, in good agreement with the value obtained from the ultra-violet spectrum. In the quantitative interpretation of the spectrum we used the values of Porter et al. [2] for the rotational and spin-orbit constants, namely $B_0=1.40827$ $cm^{-1}$, $A=77.11$ $cm^{-1}$.

In ClO [6] and NS [7] (see previous chapter) as in other good case (a) $^2\Pi_{3/2}$ molecules, it has been shown that only the axial component (h) of the total hyperfine interaction can be determined from the e.p.r. spectrum. This component is given by :

$$h = g_N \beta \beta_N \left\langle \frac{2}{r^3} \right\rangle_L + \frac{4\pi g}{3} \psi^2(0) + g \left\langle \frac{3\cos^2\theta - 1}{2r^3} \right\rangle_S \qquad (7.1)$$

where the three terms arise from the nuclear spin-electron orbital interaction, the Fermi contact interaction, and the nuclear spin-electron spin dipolar interaction. Initially the spectrum was interpreted by adjusting the values of h and $g' = 0.4g_r + 0.4\delta g_L + 0.2\delta g_s$ (the rotational and relativistic corrections to the overall g-value). The matrix representing the effective Hamiltonian was set up in a Hund's case (a) basis set with decoupled nuclear spin, including rotational levels up to $J=9/2$ for the $^2\Pi_{3/2}$ state and $J=7/2$ for the

$^2\Pi_{1/2}$ state. The matrix was diagonalised numerically for values of the magnetic field a few gauss either side of the observed fields and after allowing for the selection rules $\Delta M_J=\pm1$, $\Delta M_I=0$, the transition fields were calculated by linear interpolation. Because of the significant magnitude of h, second order corrections to the energy from states with $\Delta M_J=\pm1$, $\Delta M_I=\mp1$ had to be included; in the final calculations, the contributions from these states were included explicitly in the matrix to be diagonalised. The best fit to the spectrum and the corresponding values of h and g' are given in table 1.

The above procedure is not entirely satisfactory in the case of CF for the following reasons. The relatively large value of $B_0/A$ means that there is substantial rotational mixing of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ fine structure states (incipient case (b) coupling). This in turn means that the effect of the non-axial component of the fluorine hyperfine interaction is by no means negligible [8], particularly since the hyperfine interaction itself is quite large. The non-axial component, b, is given by :

$$b = gg_N\beta\beta_N\left\{\frac{8\pi}{3}\psi^2(0) - \left\langle\frac{3\cos^2\theta - 1}{2r^3}\right\rangle_S\right\} \qquad (7.2)$$

and its observable effect on the J=3/2 spectrum is the same as that produced by a change in the value of h. Consequently, the J=3/2 spectrum can be quantitatively interpreted in terms of a series of values of h and b, shown in figure 3. Fortunately the J=5/2 spectrum yields a second relationship between the two hyperfine parameters, from which the individual values can be estimated.

The J=5/2 spectrum has an effective g-value close to 0.34. It consists of ten lines, the five $\Delta M_J = \pm 1$ transitions being split into doublets by the fluorine hyperfine interaction. Only the six lowest field lines come within the range of our magnet. The spectrum was analysed in the same way as before, except that larger matrices were diagonalised, the $^2\Pi_{3/2}$ J=11/2 and the $^2\Pi_{1/2}$ J=9/2 levels being included. In the J=5/2 level the rotational mixing of the fine structure states is larger than in the J=3/2 level so that the relative contribution of b to the hyperfine splitting is increased. The values of h and b which best fit the J=5/2 spectrum are shown in figure 3.

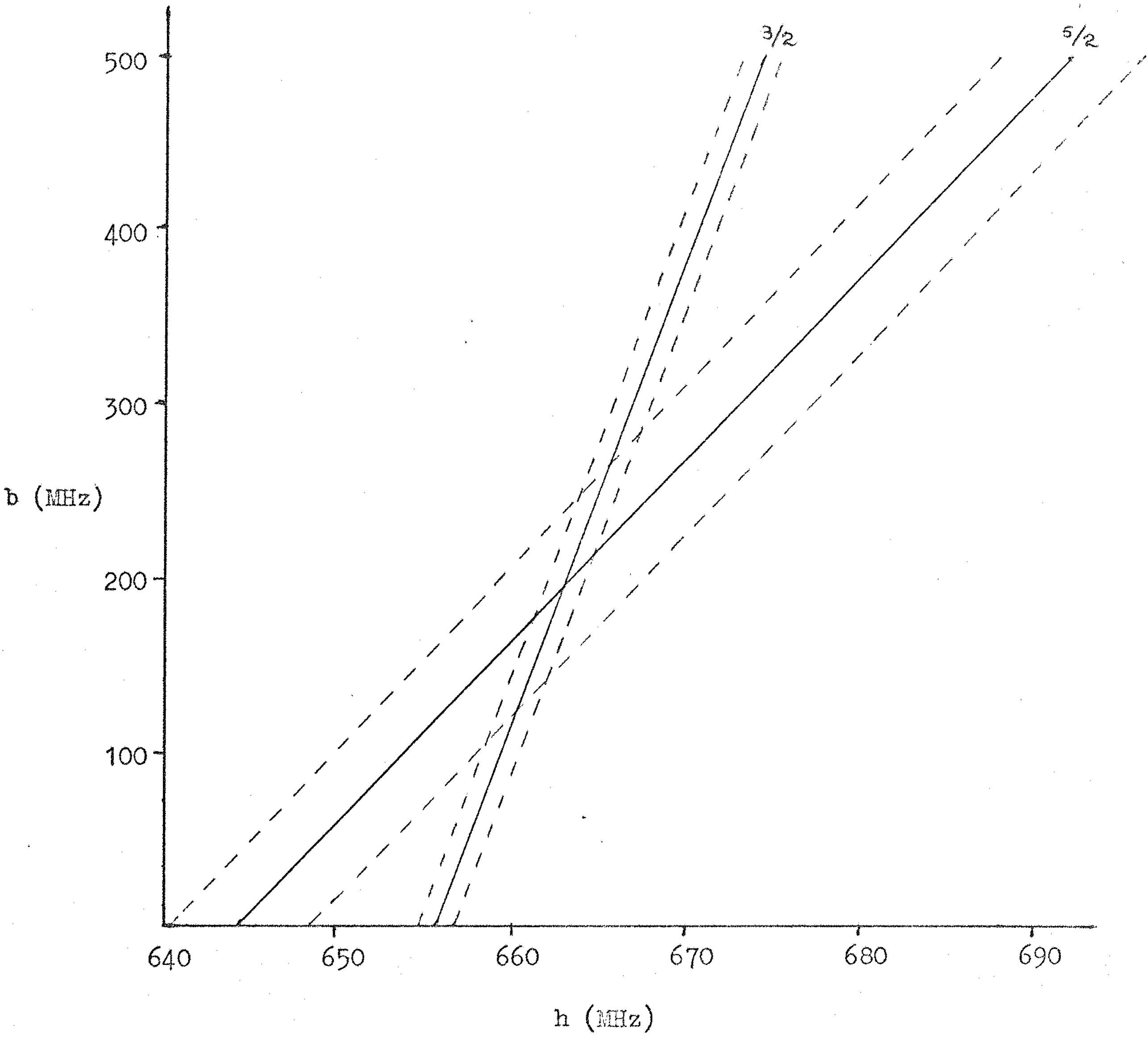
The point of intersection of the two lines in figure 3 yields unique values of h and b, which are given below.

$$h = 662.9 \pm 3 \text{ MHz}, \quad b = 190 \pm 50 \text{ MHz}$$

The errors quoted arise from the experimental errors in measuring the hyperfine splittings. The calculated fields for the absorption lines of the J=3/2 and the J=5/2 spectra using these values are given respectively, in tables 1 and 2.

The dipole moment of CF was calculated from the observed

Figure 7.3 Plot of the values of the hyperfine parameters h and b which fit the observed fluorine hyperfine splittings in the J=3/2 and 5/2 levels. The dotted lines indicate the error limits. The point of intersection gives the true value of h and b.



Stark splitting of the $M_J = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions of the J=3/2 spectrum using the expression obtained in the previous chapter for NS.

$$\Delta\varepsilon = 0.8\mu E - 0.219\mu E\left(\frac{2\beta H}{5B}\right)^2 + \frac{2.5\,\delta^2}{\mu E}, \qquad (7.3)$$

where $\delta$ is the $\Omega$-doubling constant. The electric field was obtained from the NO splitting, using the above equation; the dipole moment[5] of NO is known to be 0.15872 Debye and its $\Omega$-doubling constant is 0.91 MHz[9]. If the $\Omega$-doubling constant of CF is assumed to be about 1 MHz (as expected from it being isoelectronic with NO), its contribution to the Stark splitting can be completely neglected at fields of about 100 volts/cm or more. The value of the electric dipole moment of CF is then found to be 0.65 ± 0.05 Debye.

## 7.4 Discussion

Since we are only able to obtain two of the hyperfine paramaters, any conclusions about the unpaired electron distribution in CF must rest on some kind of approximation. Elimination of the Fermi-contact term from (7.1) and (7.2) yields :

$$\begin{aligned}(2h - b) &= g_N\beta\beta_N\left\{4\left\langle\frac{1}{r^3}\right\rangle + 3g\left\langle\frac{3\cos^2\theta - 1}{2r^3}\right\rangle\right\} \qquad (7.4)\\ &= 1136 \text{ MHz}\end{aligned}$$

The molecular orbital containing the unpaired electron can be written, approximately, as a linear combination of the carbon and fluorine 2p atomic orbitals :

$$\psi = a_F \, 2p_F - a_C \, 2p_C \tag{7.5}$$

In the region of the fluorine nucleus, where $r^{-3}$ is most important, the wave-function is expected to resemble the fluorine 2p-orbital so that we can write :

$$\left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle_S = -\frac{2}{5} \left\langle \frac{1}{r^3} \right\rangle_S \tag{7.6}$$

The hyperfine constants of NO suggest that this is obeyed to about 5%. Then putting g=2 and assuming that the expectation value of $r^{-3}$ is the same for spin and orbital motion, one obtains :

$$g_N \beta \beta_N \left\langle \frac{1}{r^3} \right\rangle = 406 \pm 20 \text{ MHz}, \quad g_N \beta \beta_N \left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle = -162 \pm 8 \text{ MHz} \tag{7.7}$$

where the error limits are those from experiment and not theory. Finally, on substituting these results into the expression for h (7.1), one obtains an approximate value for the Fermi contact interaction :

$$\frac{8\pi}{3} g g_N \beta \beta_N \psi^2(0) = 28 \pm 60 \text{ MHz} \tag{7.8}$$

In the fluorine atom itself, the value of $g_N \beta \beta_N \langle r^{-3} \rangle$ is 1900 MHz [10]. The exact value actually depends upon whether the expectation value is taken over the orbital or spin density distribution, but in our approximation the two values are necessarily the same. Then neglecting the contributions of the carbon 2p atomic orbital to $\langle r^{-3} \rangle$, we obtain :

$$a_F^2 = \frac{406}{1900} = 0.21 , \qquad a_F = 0.46 \tag{7.9}$$

The fluorine atom spectrum also yields the value of the Fermi contact term as 303 MHz, and under the assumption that the fluorine s orbital polarization is simply proportional to $a_F^2$, the predicted value of the Fermi term in CF is 65 MHz, which is within the range of the observed value. These arguements are, of course, extremely crude but they are supported by analogous data on the spin-orbit constant of CF. Dixon and Kroto [11] considered an L.C.A.O. wave-function like (7.5) and since the major contribution to the spin-orbit coupling constants comes from the unpaired electron density near the nuclei, they obtained the result :

$$A_{CF} = a_C^2 |A_c| + a_F^2 |A_F| \tag{7.10}$$

Here we shall only take the modulus of A since its sign depends upon whether the orbitals are half filled or not. Also since the value for carbon is taken from a $^3P$ state, it must be multiplied by a factor of 2 in order to represent the same quantity. Then using the values $|A_F| = 269$ cm$^{-1}$ and $|A_C| = 28$ cm$^{-1}$ and assuming $a_F^2 + a_C^2 = 1$ :

$$a_F^2 = 0.20_4 \; ; \qquad a_F = 0.42 \tag{7.11}$$

This is remarkably good agreement considering the crudity of the assumptions but it is presumably because only those parts of the electronic wave-function in close proximity to the nucleus are considered in each case and these are likely to be very similar to the atomic orbitals. Although these results provide a worthwhile indication of the unpaired electron distribution in CF, accurate wave-functions are necessary for a really accurate discussion of the hyperfine results.

The electric dipole moment of CF is found to be much larger than the isoelectronic NO, as expected on electro-negativity grounds. The sign of the dipole moment cannot be determined from these experiments but is expected to be consistent with the polarity $C^+-F^-$.

## References to Chapter 7

1. E. B. Andrews and R. F. Barrow, Nature, Lond., 165, 890 (1950); Proc. Phys. Soc. A64, 481 (1951).
2. T. L. Porter, D. E. Mann and N. Acquista, J. Mol. Spec. 16, 228 (1965).
3. A. Carrington, D. H. Levy and T. A. Miller, Rev. Sci. Instr. 38, 1183 (1967).
4. A. Carrington, D. H. Levy and T. A. Miller, J. Chem. Phys. 47, 3801 (1967).
5. W. Klemperer and R. M. Neumann, (Private communication, 1969).
6. A. Carrington, P. N. Dyer and D. H. Levy, J. Chem. Phys. 47, 1756 (1967).
7. A. Carrington, B. J. Howard, D. H. Levy and J. C. Robertson, Mol. Phys. 15, 187 (1968).
8. H. Uehara and Y. Morino, Mol. Phys. 17, 239 (1969).
9. R. L. Brown and H. E. Radford, Phys. Rev. 147, 6 (1966).
10. J. S. M. Harvey, Proc. Roy. Soc. A285, 581 (1965).
11. R. N. Dixon and H. W. Kroto, Trans. Far. Soc. 59, 1484 (1963).

# Chapter 8

# The Renner Effect

## 8.1 Introduction

In linear molecules with a doubly-degenerate electronic state ($\Pi$, $\Delta$, etc. ), it is possible, when a doubly degenerate bending mode of vibration is excited, to have a coupling between the electronic and vibrational motion of the molecule. This removes some of the expected four-fold degeneracy and ensures that the Born-Oppenheimer product wave-function is no longer a valid approximation for some of the states; such an interaction was first considered by Renner[1] and is called the Renner or Renner-Teller effect.[2] This can be immediately illustrated by a group theoretical arguement. The bending-vibrational and electronic wave-functions belong to degenerate representations of the $C_{\infty v}$ (or $D_{\infty h}$) symmetry group. The vibronic wave-functions belong to the direct product representation, which is in general reducible. For example :

$$\Pi \times \Pi = \Sigma^+ + \Sigma^- + \Delta \tag{8.1}$$

Renner set up the problem for a molecule in a $\Pi$ state by assuming that on bending it acquired a dipole moment which mixed in excited states. Using second-order perturbation theory, he showed that the resulting interaction is equivalent to an extra term in the

Hamiltonian of the form $\varepsilon k Q_2^2 \cos 2(\theta-\phi)$, where $\theta$ and $\phi$ are respectively the electronic and vibrational azimuthal angles, and $Q_2$ is the bending normal coordinate.

In an alternative approach, Pople and Longuet-Higgins [3,4] have expanded the vibrational potential as a power series in $Q_2$ and $\cos(\theta-\phi)$ like :

$$E_{vib} = V_1 Q_2 \cos(\theta-\phi) + V_2 Q_2^2 \cos 2(\theta-\phi) + \cdots \quad (8.2)$$

From this they extract the second term, which gives a diagonal contribution in a $\Pi$ electronic state, and neglect all second order effects. Further theoretical investigations have been made by Pople [5] into the effects of also introducing spin-orbit coupling in $^2\Pi$ molecules. Finally the effect of the Renner perturbation on the rotational structure of a linear triatomic molecule in a $^2\Pi$ or a $^3\Pi$ electronic state has been considered by Hougan [6-8].

The recent discovery of the e.p.r. spectrum of the linear triatomic radicals NCO [9,10] and NCS [11], both with $^2\Pi$ ground electronic states has renewed interest in the Renner effect. The theoretical results obtained in the papers mentioned above are strictly speaking only applicable to the investigation of electronic spectra; a more precise derivation of the Renner effect is necessary for the interpretation of high resolution spectra in the microwave or radio-frequency region.

In this chapter, the Coulombic interaction for the bending mode of vibration will be expanded as a power series in $Q_2$ (the normal bending coordinate) and both first and second order contributions to the Renner effect will be included in an effective Hamiltonian. Because of the large mixing in of excited electronic states, it is discovered that there are important third order contributions to the observed magnetic moment of the molecule. The theory predicts that the correction to the orbital g-value should be linear in the vibrational quantum number, $v_2$, and this has been confirmed by the experimental results.

## 8.2 Basic Theory

The problem of the linear triatomic molecule cannot be solved by using the Born-Oppenheimer seperation of electronic and nuclear motions, except in the linear configuration ($Q_2 = 0$). Then the potential due to the nuclei has cylindrical symmetry and the electronic wave-function can be classified by the quantum number $\Lambda$, representing the expectation value of the orbital angular momentum. This wave-function $\psi_e(\Lambda; r_i, r'_\alpha)$ is a solution of the electronic Hamiltonian, $\mathcal{H}_e$ :

$$\mathcal{H}_e \psi_e(\Lambda; r_i, r') = \sum_i \frac{1}{2m} p_i^2 + \sum_{i \neq j} \frac{e^2}{2r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{r_{i\alpha}} \psi_e$$

$$= E_e \psi_e(\Lambda; r_i, r'_\alpha) \qquad (8.3)$$

where $\underline{r}'_\alpha$ is the coordinate of the nuclei on the linear axis.

When the molecule bends, the Coulombic potential energy must be modified; the resulting perturbation to the electronic-nuclear energy is :

$$V(Q_2) - V(0) = \frac{-Z_\alpha e^2}{\left[(z_i-z_\alpha)^2 + \rho_i^2 + \rho_\alpha^2 - 2\rho_i\rho_\alpha\cos(\theta_i-\phi_\alpha)\right]^{\frac{1}{2}}} + \frac{Z\,e^2}{\left[(z_i-z_\alpha)^2 + \rho_i^2\right]^{\frac{1}{2}}} \qquad (8.4)$$

where the cylindrical polar coordinates ($\rho$, $\theta$ or $\phi$, z) have been used. Now assuming small-amplitude vibrations so that $\rho_\alpha^2 < (z_i-z_\alpha)^2 + \rho_i^2$, the perturbation can be written as a power series in $\rho_\alpha$ and $\cos(\theta_i-\phi_\alpha)$. Then if we replace $(z_i-z_\alpha)^2 + \rho_i^2$ by f(e), which is only a function of the electronic position coordinates or the stretching normal coordinates, the perturbation to the Coulombic energy is :

$$V(Q_2) - V(0) = \frac{Z_\alpha e^2}{f^{\frac{1}{2}}(e)}\,\frac{\rho_\alpha^2 - 2\rho_i\rho_\alpha\cos(\theta_i-\phi_\alpha)}{2f(e)} - \frac{3Z_\alpha e^2\left\{\rho_\alpha^2 - 2\rho_i\rho_\alpha\cos(\theta_i-\phi_\alpha)\right\}^2}{8\,f^{\frac{1}{2}}(e)\;f^2(e)} + \text{higher order terms} \qquad (8.5)$$

The problem of the configuration,in which $\rho_\alpha^2 \geqslant (z_i-z_\alpha)^2 + \rho_i^2$, are briefly discussed in appendix C, but do not invalidate the arguements to be given below.

It is desirable to replace all the bending coordinates of the nuclei by the normal coordinate $Q_2$.

$$\rho_\alpha = \ell_{\alpha 2} Q_2 \; ; \quad \phi_\alpha = \phi \qquad \text{for all } \alpha \qquad (8.6)$$

Then collecting all the electron-nuclear Coulombic interactions together, the total bending perturbation can be written as :

$$V(Q_2) - V(0) = \sum_i \Big( A_1(e_i)\, Q_2 + A_2(e_i)\, Q_2^2 + A_{11}(e_i) Q_2 \cos(\theta_i - \phi) + A_{22}(e_i)\, Q_2 \cos 2(\theta_i - \phi) \Big) + \text{higher order terms} \qquad (8.7)$$

The coefficients, A, are functions of mainly the electronic coordinates with a slight dependence on the stretching normal coordinates. Included in these terms are also the perturbations obtained from expanding the nuclear-nuclear Coulombic interaction as a power series in $Q_2$.

The total Hamiltonian, which can be written as :

$$\mathcal{H} = \mathcal{H}_e + \sum_r \tfrac{1}{2} P_r^2 + V(Q_2) - V(0) = \mathcal{H}_e + \mathcal{H}_n \qquad (8.8)$$

mixes the different electronic states. We are interested in measuring spectra in the ground electronic state, in the ground stretching-vibrational state and in any of the lower states of the bending vibrational manifold; this will be called the "ground vibronic manifold" for simplicity. In order to solve for the energy levels, it is desirable to derive an effective Hamiltonian, which operates in just this particular manifold. As before this is most easily performed by the technique of degenerate perturbation theory [14,15]. $P_0$ is defined as the projection operator onto the ground vibronic manifold, $|0,i\rangle$ :

$$P_0 = \sum_i |0,i\rangle\langle 0,i| \tag{8.9}$$

where i represents all the other quantum numbers necessary to specify the state (including the bending vibrational quantum number, $v_2=n-1$). We also define :

$$\frac{Q_0}{a^r} = \sum_{t\neq 0}\sum_i \frac{|t,i\rangle\langle t,i|}{(E_0-E_t)^r} \tag{8.10}$$

Following Bloch [14], the effective Hamiltonian may be written to third order in the form :

$$\begin{aligned}\mathcal{H}_{eff} = {} & P_0\mathcal{H}_e P_0 + P_0\mathcal{H}' P_0 + P_0\mathcal{H}'(Q_0/a)\mathcal{H}'P_0 \\ & + P_0\mathcal{H}'(Q_0/a)\mathcal{H}'(Q_0/a)\mathcal{H}'P_0 - P_0\mathcal{H}'(Q_0/a^2)\mathcal{H}'P_0\mathcal{H}'P_0 \\ & + \text{higher order terms}\end{aligned} \tag{8.11}$$

$\mathcal{H}'$ should be thought of as $\mathcal{H}_n$, from (8.8), plus all the smaller magnetic interactions to be introduced later (see equation 5.17). In the expansion, we shall limit ourselves to the harmonic approximation which is generally sufficiently accurate to explain effects in the lower vibrational states. The first two terms in (8.11) are those parts of the Hamiltonian that give diagonal contributions in the ground manifold. Then, for the moment, taking $\mathcal{H}' = \mathcal{H}_n$ :

$$\mathcal{H}^1_{\mathrm{eff}} = \mathcal{H}_e + \sum_r \tfrac{1}{2}P_r^2 + A_2 Q_2^2 + A_{22} Q_2^2\cos(\theta-\phi)2 + O(Q_2^3) , \qquad (8.12)$$

where $\theta$ is used instead of $\theta_i$ to signify all electrons (it has the same selection rules on matrix elements if the electronic wave-functions are assumed to have the form $\exp i\Lambda\theta$), and the sum over r means the sum over the bending modes if the energy of the ground states of the stretching vibrations is included in $\mathcal{H}_e$.

The second order contributions of (8.11) are obtained from those terms in the perturbation (8.7) that are linear in $Q_2$; they result in

$$\mathcal{H}^2_{\mathrm{eff}} = (a_2 + a_2') Q_2^2 + a_{22} Q_2^2 \cos 2(\theta-\phi) \qquad (8.13)$$

where $a_2$ and $a_{22}$ are obtained from the mixing of excited states with $\Lambda$ changed by 1, and $a_2'$ from the mixing in of excited vibrational or electronic states with the same value of $\Lambda$.

$$a_2 = -\tfrac{1}{4} \sum_{p=\pm 1} \sum_{\substack{\Lambda= \\ \Sigma \text{ or } \Delta}} (E_\Lambda - E_0)^{-1} \langle \Pi^o_{\pm 1} | A_{11} e^{ip\theta} | \Lambda \rangle \langle \Lambda | A_{11} e^{-ip\theta} | \Pi^o_{\pm 1} \rangle \tag{8.14}$$

where the suffix $\pm 1$ is given to the $\Pi^o$ state to indicate its value of $\Lambda$.

$$a_{22} = -\tfrac{1}{2} \sum_{\Lambda = \Sigma} (E - E_0)^{-1} \langle \Pi^o_{\pm 1} | A_{11} e^{\pm i\theta} | \Sigma \rangle \langle \Sigma | A_{11} e^{\pm i\theta} | \Pi^o_{\mp 1} \rangle \tag{8.15}$$

and

$$a_2' = - \sum_t (E_t - E_o)^{-1} \langle \Pi^o | A_1 | \Pi^t \rangle \langle \Pi^t | A_1 | \Pi^o \rangle \tag{8.16}$$

$a_2$ and $a_2'$ contribute, in second order, to the harmonic vibrational potential and $a_{22}$ is a second order contribution to the Renner coupling. Collecting all such terms together, the vibrational part of the effective Hamiltonian, rewritten in polar coordinates, becomes:

$$\mathcal{H}_{eff} = \frac{1}{2Q_2^2}\left[(Q_2P_2)^2 + P_\phi^2\right] + \tfrac{1}{2}k_2Q_2^2 + \varepsilon k_2 Q_2^2 \cos 2(\theta - \phi) \tag{8.17}$$

where

$$\tfrac{1}{2}k_2 = \langle A_2 \rangle + a_2 + a_2' \tag{8.18}$$

$$k_2 = \langle A_{22} \rangle + a_{22} \tag{8.19}$$

and

$$\langle A_1 \rangle = 0 , \tag{8.20}$$

if the molecule has a linear equilibrium configuration

In the absence of the Renner coupling terms, the

Hamiltonian is that for the two-dimensional isotropic harmonic oscillator [16]. Its solutions are of the form :

$$\chi(n,l) = \rho_{n|l|}(Q_2) \exp il\phi \qquad (8.21)$$

and it has eigenvalues, $nh\nu_2 = (v_2+1)h\nu_2$, where $\nu_2$ is the bending-vibrational frequency. The second quantum number, l, signifies the vibrational angular momentum about the figure axis and can take the values $v_2, v_2-2, \ldots\ldots, -v_2$. Since the magnitude of $\varepsilon$ is usually less than unity, the functions in (8.21) are found to be a suitable representation for evaluating the Renner effect.

So far no account has been taken of the spin-orbit, rotational and Zeeman perturbations. Their first and second order contributions may be obtained in exactly the same manner as for diatomic molecules in chapter 5, yielding :

$$\begin{aligned} \mathcal{H}'_{\mathrm{eff}} = P_0\Big\{ & B'(\underline{J}-\underline{G}-\underline{L}-\underline{S})^2 + g_S\beta\underline{H}.\underline{S} + g_L\beta H_z L_z + A'L_zS_z \\ & + \sum_{q=\pm1}(-1)^q\Big[\Delta g_S\beta T^1_q(\underline{H})T^1_{-q}(\underline{S}) + \gamma' T^1_q(\underline{J}-\underline{S})T^1_{-q}(\underline{S}) \\ & + g_r\beta T^1_q(\underline{H})T^1_{-q}(\underline{J}-\underline{S})\Big] + \lambda' T^2_0(\underline{S}) \\ & + \mathcal{H}_{\mathrm{hyp}} + \mathcal{H}_Q + \mathcal{H}_{NZ} + \mathcal{H}_E\Big\}P_0 \end{aligned} \qquad (8.22)$$

It is also necessary to consider the second order cross-terms between the spin-orbit, rotational, and Zeeman interactions and the Coulombic perturbation. The resulting terms have the form :

$$\mathcal{H}''_{\mathrm{eff}} = \sum_{q=\pm 1} (-1)^q \Big\{ \tau T^1_q(\underline{S}) Q_2 e^{-iq\phi} + \xi T^1_q(\underline{J}-\underline{S}) Q_2 e^{-iq\phi} + g^e_G \beta T^1_q(\underline{H}) Q_2 e^{-iq\phi} \Big\} \tag{8.23}$$

where

$$\tau = \sum_n \sum_{q=\pm 1} \tfrac{1}{2}(E - E_0)^{-1} \Big\{ \langle \ell_0 | A T^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | A_{11} e^{-qi\theta} | \ell_0 \rangle + \langle \ell_0 | A_{11} e^{iq\theta} | \ell_n \rangle \langle \ell_n | A T^1_{-q}(\underline{L}) | \ell_0 \rangle \Big\} \tag{8.24}$$

$$\xi = \sum_n \sum_{q=\pm 1} \tfrac{1}{2}(E - E_0)^{-1} \Big\{ \langle \ell_0 | B T^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | A_{11} e^{-iq\theta} | \ell_0 \rangle + \langle \ell_0 | A_{11} e^{iq\theta} | \ell_n \rangle \langle \ell_n | B T^1_{-q}(\underline{L}) | \ell_0 \rangle \Big\} \tag{8.25}$$

$$g^e_G = \sum_n \sum_{q=\pm 1} \tfrac{1}{2}(E - E_0)^{-1} \Big\{ \langle \ell_0 | T^1_q(\underline{L}) | \ell_n \rangle \langle \ell_n | A_{11} e^{-iq\theta} | \ell_0 \rangle + \langle \ell_0 | A_{11} e^{iq\theta} | \ell_n \rangle \langle \ell_n | T^1_{-q}(\underline{L}) | \ell_0 \rangle \Big\} \tag{8.26}$$

None of these terms give diagonal contributions to the energy but all mix states with $\Delta n=\pm 1, \Delta l=\pm 1$. Strictly speaking these terms should be included in any matrix representing the Hamiltonian, but, ignoring the contributions arising from the cubic terms ($k'Q_2^3$) in the vibrational potential, all their contributions have the same form as terms already in (8.22). Then as long as the spin-rotation constant, rotational g-factor etc. are used as just parameters, which can include all these and other second order effects, $\mathcal{H}''_{\mathrm{eff}}$ may be completely neglected.

In the complete Hamiltonian (3.202 to 3.214) there are several small vibrational interactions not present in diatomic molecules, namely the spin-vibration, orbit-vibration and vibrational Zeeman interaction. The coefficients of the first two are typically of the order of 100 MHz (the same order of magnitude as the spin-rotation interaction) and, since they are competing with the spin-orbit coupling in trying to modify the e.p.r. spectra, their effect may be neglected in a particular vibrational state of a case (a) molecule. There may be a measurable effect if the molecule approximates to a case (b) coupling scheme.

The vibrational Zeeman term can have a significant effect on the e.p.r. spectrum. If it is written in the equivalent form :

$$\mathcal{H}_{VZ} = - g_G^N \beta\, \underline{G}\cdot\underline{H} \qquad (8.27)$$

where $\underline{G}$ is the vibrational angular momentum ($G_z$=l), it can be seen that the g-value of a vibrational level changes with l.

Since we are working in the ground vibronic manifold, it is also necessary to second order contributions to the effective Hamiltonian from the terms :

$$-B \sum_{q=\pm 1} (-1)^q T^1_q(\underline{J}-\underline{S}) T^1_{-q}(\underline{G}) \qquad (8.28)$$

This connects different stretching vibrational states [17] and as a consequence yields another second order contribution to the rotational constant.

The Hamiltonian derived so far is essentially that obtained by taking the theory for diatomic molecules, with the obvious vibrational modifications, to explain the spectra of linear triatomic molecules. However some important corrections have been omitted. The mixing of electronic states by the bending vibration is so strong that certain third order contributions to the effective Hamiltonian may be expected to have a significant magnitude. Since such terms involve the electronic energy squared in the denominator, only combinations of perturbations which involve the bending perturbation or spin-orbit coupling squared need be considered. In the NCO and NCS radicals, the spin-orbit coupling constant, A, is only of the order of 200 $cm^{-1}$, so that with an excitation energy of the order of 20,000 $cm^{-1}$ its contributions will be neglected. The effects of large values of A on the spectra of diatomic molecules will be considered in the next chapter.

In this work we are mainly interested in the Zeeman effect of gaseous radicals so that it is likely that those third order terms in which one of the matrix elements involves the Zeeman interaction will be most important. The only terms which will give a diagonal contribution are :

$$\mathcal{H}^3_{\text{eff}} = \sum_{\Lambda} (E_\Lambda - E_0)^{-2} |\Pi^0\rangle\langle\Pi^0| A_{11} Q_2 \cos(\theta-\phi) |\Lambda\rangle\langle\Lambda| A_{11} Q_2 \cos(\theta-\phi) |\Pi^0\rangle$$

$$\times\ \beta T^1_0(\underline{H}) \Big[\langle\Lambda| g_L T^1_0(\underline{L}) + g_s T^1_0(\underline{S}) |\Lambda\rangle \qquad (8.29)$$

$$- \langle\Pi^0| g_L T^1_0(\underline{L}) + g_s T^1_0(\underline{S}) |\Pi^0\rangle\Big] \langle\Pi^0|$$

The diagonal contributions of $T^1_0(\underline{S})$ are the same in both the ground and excited electronic states and may be omitted. The remaining terms (diagonal in $\Lambda$) may be represented in an effective Hamiltonian by the expression :

$$\mathcal{H}^3_{\text{eff}} = \Delta g_L \beta T^1_0(\underline{H}) T^1_0(\underline{L}) \frac{k_2 Q_2^2}{h\nu_2} = n\, \Delta g_L \beta\, T^1_0(\underline{L}) T^1_0(\underline{H}) \quad (8.30)$$

where $$\frac{\Delta g_L k_2}{h\nu_2} = \frac{1}{4} \sum_{q=\pm 1} \sum_{\Lambda} (-1)^{\delta} \langle\Pi^0| A_{11} e^{iq\theta} |\Lambda\rangle\langle\Lambda| A_{11} e^{-iq\theta} |\Pi^0\rangle\, (E_\Lambda - E_0)^{-2} \quad (8.31)$$

in which $\delta$ is odd for $\Lambda$ representing $\Sigma$ states and even for $\Delta$ states. This predicts that the orbital g-factor must be changed linearly with n in order to interpret the e.p.r. spectrum in different vibrational levels. The work on the first three bending-vibrational levels of NCO [12,13] has confirmed this theory.

If the excited state is a $\Sigma$ state, it is possible to connect the $\Lambda = \pm 1$ components of a $\Pi$ state in the same way as the Renner coupling term in (8.15). This term can be written in the form :

$$\mathcal{H}^{3'}_{\mathrm{eff}} = \Delta g'_L \beta T^1_0(\underline{L}) T^1_0(\underline{H}) \frac{k_2 Q_2^2}{h\nu_2} \cos 2(\theta - \phi) \qquad (8.32)$$

This a further correction to the orbital g-factor in states in which strong Renner mixing can occur ($|l|+1<n$, see next section).

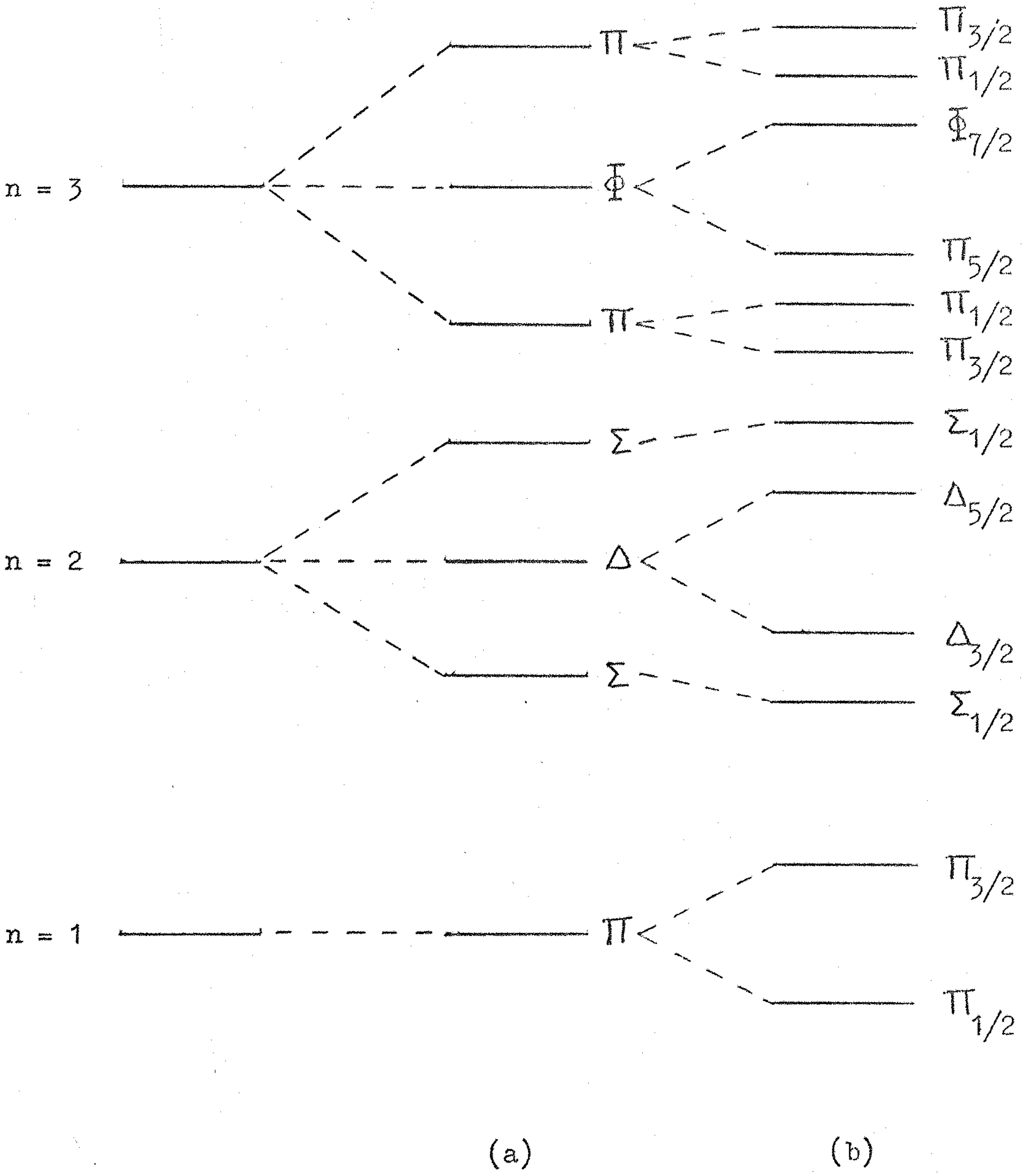
## 8.3 Vibronic and Fine Structure of Molecules with a $^2\Pi$ Electronic State

Before a detailed consideration of the e.p.r. spectra of linear triatomic molecules, it is useful to briefly consider the vibronic energy levels.

In the absence of the Renner effect, the electronic states can be classified by the quantum numbers $\Lambda(=\pm 1)$ and $\Sigma\ (=\pm\frac{1}{2})$, respectively the component of orbital and spin angular momentum along the internuclear axis. As mentioned before the bending vibrational wave-function is that of the two-dimensional isotropic harmonic oscillator and is specified by n and l; n is the energy of the vibrational state in units of the vibrational quantum and l is the vibrational angular momentum ($l=n-1, n-3, \cdots, -n+1$). The energy levels are shown on the left-hand side of figure 1.

The Renner coupling term, $\varepsilon k_2 Q_2^2 \cos 2(\theta-\phi)$ has finite matrix elements between states with $\Delta\Lambda=\pm 2$, $\Delta l=\pm 2$, and $\Delta n=0$ or $\pm 2$. Consequently, for $|l| \neq n-1$, $\Lambda$ and l are no longer good quantum numbers, although the total angular momentum component along the figure axis, $K = \Lambda + l$, is still conserved. These vibronic states

Figure 8.1 The vibrational energy levels split by (a) the Renner effect alone, (b) the Renner effect and spin-orbit coupling



are labelled as $\Sigma$, $\Pi$, $\Delta$, $\Phi$ .... according as K =0,1,2,3 .... It should be noted that states with the maximum value of K in a given vibrational level are only slightly changed in energy, through the second order mixing of states with $\Delta n=2$. All other states are considerably split, because the mixing of states in the same vibrational level can occur in first order. Neglecting the small second order contributions, the energies of the vibronic levels may be sumarised by :

$$E_{n,K} = \left[n \pm \tfrac{1}{2}\varepsilon(n^2 - K^2)^{\frac{1}{2}}\right] h\nu_2 \tag{8.33}$$

These are represented in column 2 of figure 1.

Every vibronic state with $|K|>0$ is further split into two by the spin-orbit coupling and the K=0 states are slightly displaced in energy. The resulting energy levels are given on the right-hand side of figure 8.1 ; the suffices,P, represent the axial component of the total angular momentum, $K+\Sigma$.

## 8.4 The e.p.r. Spectra of Linear Triatomic Molecules.

Recently, Carrington, Fabris and Lucas have observed the e.p.r. spectrum of NCO in its $^2\Pi_{3/2}$ ground vibronic state [9] and also its $^2\Delta_{5/2}$ [10] and $^2\Phi_{7/2}$ vibronic states; these last two are from, respectively, the first and second excited vibrational levels. All these have the maximum value of K and are essentially good Born-

Oppenheimer states (i.e. they can be represented by the product of an electronic and a nuclear wave-function, to a high approximation). If the molecule can be considered to closely approximate to a Hund's case (a) coupling scheme, the g-value of the spectrum in the rotational state with angular momentum, J, is given by :

$$g = \frac{(g_L\Lambda + g_s\Sigma)\ P}{J(J+1)} \tag{8.34}$$

i.e. 0.8000, 0.5714, and 0.4444, respectively, in the ground rotational level of the $^2\Pi_{3/2}$, $^2\Delta_{5/2}$ and $^2\Phi_{7/2}$ vibronic states.

The observed g-values of the spectra differ from this for several reasons.

Firstly, as in diatomic molecules, the second order mixing of the fine-structure states and the higher order Zeeman mixing of the rotational states can affect the g-value. The expressions for the $^2\Pi_{3/2}$ state are the same as those in (6.7) and (6.8). Slightly different expressions must be used for the $^2\Delta_{5/2}$ and $^2\Phi_{7/2}$ states; their modified g-values at 9270 MHz are given in table 8.1.

Secondly, there is the Renner mixing of vibronic states with the same value of K, but with $\Delta n=2$. The state $|n=n, l=l, \Lambda=1, \Sigma=\frac{1}{2}\rangle$ is mixed with $|n+2, l+2, -1, \frac{1}{2}\rangle$ and for l=n-1 the matrix element connecting the two states is $\frac{1}{2}\varepsilon\left[K(K+1)\right]^{\frac{1}{2}}h\nu_2$. The latter state has the orbital angular momentum reversed and in third order contributes a correction of $-\varepsilon^2K(K+1)g_L/8$ to the orbital g-factor. After

Table 8.1 Various contributions to the observed g-value of the NCO radical in its three lowest vibrational levels.

| Contribution to g-factor | $^2\Pi_{3/2}$ <br> $n = 1$ , $J = 3/2$ | $^2\Delta_{5/2}$ <br> $n = 2$ , $J = 5/2$ | $^2\Phi_{7/2}$ <br> $n = 3$ , $J = 7/2$ |
|---|---|---|---|
| Observed | 0.7909 | 0.5638 | 0.4356 |
| First order | 0.8000 | 0.5714 | 0.4444 |
| Higher order terms (as in a diatomic molecule) | 0.7952 | 0.5713 | 0.4456 |
| Renner Effect | 0.7932 | 0.5668 | 0.4388 |
| Residual $= \frac{\Delta g_L}{(J+1)}$ | -0.0023 | -0.0030 | -0.0032 |
| $\Delta g_L$ | -0.0058 | -0.0053 | -0.0048 |
| Value of $\Delta g_L$ using $\varepsilon = -0.150$ | -0.0063 | -0.0063 | -0.0061 |

making this correction (see table 8.1), there is still a discrepancy between the calculated and observed g-factors. This can be accounted for by the third order correction $n\Delta g_L$ to the orbital g-factor. The value of $\Delta g_L$ calculated from each vibronic level is given in table 8.1 and is fairly constant, supporting the theory. The rotational and vibrational g-factors have not been included and these could account for the slight difference in the calculated values of $\Delta g_L$. Alternatively the agreement can be improved by slightly modifying the value of $\varepsilon$.

## 8.5 Relationship between $\Delta g_L$ and $\varepsilon$

Since $\Delta g_L$ and the second order contribution to the Renner constant both involve the mixing of excited electronic states, it seems reasonable that they should be related.

The g-value correction $\Delta g_L$ is obtained from terms of the form $\langle \Pi^o_{\pm 1} | A_{11} e^{iq\theta} | \Sigma \text{ or } \Delta \rangle \langle \Sigma \text{ or } \Delta | A_{11} e^{-iq\theta} | \Pi^o_{\pm 1} \rangle$. Since the two matrix elements are the complex conjugate of one another, the product must be real and positive. Then from (8.31), the contribution to $\Delta g_L$ from $\Delta$ states is positive while that from $\Sigma$ states is negative. For NCO [10], the observed value of $\Delta g_L$ is -0.006, so that on omitting the effect of $\Delta$ states, the sum of the contributions to $\Delta g_L$ from $\Sigma^+$ and $\Sigma^-$ states is given by :

$$\Delta g_L^+ + \Delta g_L^- \leqslant -0.006 \qquad (8.35)$$

In order to relate these to the second order contributions to $\varepsilon$, it is necessary to consider the effect of the space inversion operator, $\mathscr{I}$, on $\langle\Sigma|A_{11}e^{\mp i\theta}|\Pi^{o}_{\pm 1}\rangle$. Under this operation the radial coordinates $\rho_i$ remain unchanged and $\theta_i$ goes to $-\theta_i$. Thus :

$$\mathscr{I}\,|\Pi^{o}_{\pm 1}\rangle \quad = \quad |\Pi^{o}_{\mp 1}\rangle \tag{8.36}$$

$$\mathscr{I}\,(A_{11}e^{\pm i\theta}) \quad = \quad A_{11}e^{\mp i\theta} \tag{8.37}$$

$$\mathscr{I}\,|\Sigma^{\pm}\rangle \quad = \quad (-1)^{s}\,|\Sigma^{\pm}\rangle \tag{8.38}$$

where s is even for $\Sigma^{+}$ states and odd for $\Sigma^{-}$ states [18]. Since the matrix elements must be invariant under the inversion operator [19]:

$$\langle\Sigma^{\pm}|A_{11}e^{\mp i\theta}|\Pi^{o}_{\pm 1}\rangle \quad = \quad (-1)^{s}\langle\Sigma^{\pm}|A_{11}e^{\pm i\theta}|\Pi^{o}_{\mp 1}\rangle \tag{8.39}$$

But the second order contributions $\varepsilon^{+}$ and $\varepsilon^{-}$ to the Renner constant (from the excited $\Sigma^{+}$ and $\Sigma^{-}$ states) are obtained from terms of the form :

$$\begin{aligned}&\langle\Pi^{o}_{\pm 1}|A_{11}e^{\pm i\theta}|\Sigma^{\pm}\rangle\langle\Sigma^{\pm}|A_{11}e^{\pm i\theta}|\Pi^{o}_{\mp 1}\rangle \\ &\qquad = \quad (-1)^{s}\langle\Pi^{o}_{\pm 1}|A_{11}e^{+i\theta}|\Sigma^{\pm}\rangle\langle\Sigma^{\pm}|A_{11}e^{\mp i\theta}|\Pi^{o}_{\mp 1}\rangle\end{aligned} \tag{8.40}$$

Thus from (8.15), $\Sigma^{+}$ states give a negative contribution and $\Sigma^{-}$ states a positive contribution to $\varepsilon$. The observed value of $\varepsilon$ in NCO is -0.159, probably due to the fact that the first excited electronic state is $\Sigma^+$. If it assumed that $\Sigma^+$ electronic states are the only $\Sigma$ states that give a significant contribution to $\Delta g_L$ and the second order Renner constant, one obtains :

$$\frac{a_{22}}{a_{22} + \langle A_{22} \rangle} \geqslant \frac{2 \quad g_L \, (E_{\Sigma^+} - E_0)}{h\nu_2} \tag{8.41}$$

where $E_{\Sigma^+}$ is the energy of the first $\Sigma^+$ state. All the parameters on the right hand side of the above expression are known for NCO, $\varepsilon = -0.159$, $h\nu_2 = 538.9 \text{ cm}^{-1}$, $\Delta g_L = -0.006$ and $\Delta E_{\Sigma^+} = 23{,}000 \text{ cm}^{-1}$. Hence :

$$\frac{a_{22}}{a_{22} + \langle A_{22} \rangle} \geqslant 3.2 \tag{8.42}$$

This not only suggests that the second order contribution to the Renner constant is the largest but that the first order contribution has the opposite sign. Simple electrostatic arguments, however, suggest that the first order contribution to $\varepsilon$ should be negative; the electrons and nuclei prefer to be in the same plane (see 8.5). This discrepancy can be overcome by including the contribution from $\Sigma^-$ states.

If $\Delta g_L^{\pm}$ is multiplied by $\Delta E$, the excitation energy to the first $\Sigma^+$ state, we obtain :

$$\Delta g_L^+ \frac{k_2}{h\nu_2} \geqslant a_{22}^+/2\Delta E \quad ; \quad \Delta g_L^- \frac{k_2}{h\nu_2} \geqslant -a_{22}^-/2\Delta E \tag{8.43}$$

where $a_{22}^{+}$ and $a_{22}^{-}$ are the contributions to $a_{22}$ from $\Sigma^{+}$ and $\Sigma^{-}$ states respectively. Therefore :

$$\frac{a_{22}^{+} - a_{22}^{-}}{k_2} \leqslant 2(\Delta E/h\nu_2)\,\Delta g_L = -0.51 \tag{8.44}$$

Then assuming $\langle A_{22} \rangle$ is negative :

$$\frac{a_{22}^{+} + a_{22}^{-}}{k_2} > -0.159 \tag{8.45}$$

Hence,

$$3.2\,(a_{22}^{+} + a_{22}^{-}) > a_{22}^{+} - a_{22}^{-}$$

and since $a_{22}^{+}$ is negative :

$$|a_{22}^{+}| < 1.95\,|a_{22}^{-}| \tag{8.46}$$

Thus the contributions from $\Sigma^{-}$ states are at least half as important as those from $\Sigma^{+}$ states and must be included in the previous considerations.

If the e.p.r. spectrum of a strongly Renner mixed state can be observed, it will be possible to also obtain $\Delta g_L'$. The expression for $\Delta g_L' k_2/h\nu_2$ is similar to that for $a_{22}$ in (8.15) except with the energy denominator squared. If one of these energy denominators can be replaced by $\Delta E$, then :

$$\Delta g_L' \approx (-a_{22}/\Delta E)\times(h\nu_2/k_2) \tag{8.47}$$

This would yield a much more accurate estimate of the relative importances of the first and second order contributions to the Renner constant.

## References to Chapter 8

1. R. Renner, Z. Phys. 92, 172 (1934).
2. G. Herzberg, "Molecular Spectra and Molecular Structure,-III. Electronic Spectra and Electronic Structure of Polyatomic Molecules". (D. Van Nostrand, N.J., 1966).
3. J. A. Pople and H. C. Longuet-Higgins, Mol. Phys. 1, 372 (1966).
4. H. C. Longuet-Higgins, Advances in Spectroscopy, 2, 429 (1961).
5. J. A. Pople, Mol. Phys. 3, 16 (1960).
6. J. T. Hougen, J. Chem. Phys. 36, 519 (1962).
7. J. T. Hougen, J. Chem. Phys. 36, 1874 (1962).
8. J. T. Hougen, J. Chem. Phys. 37, 403 (1962).
9. A. Carrington, A. R. Fabris and N. J. D. Lucas, J. Chem. Phys. 49, 5545 (1968).
10. A. R. Fabris, Ph.D. Thesis, (Southampton, 1970).
11. A. Carrington, A. R. Fabris and N. J. D. Lucas, Mol. Phys. 16, 195 (1968)
12. A. Carrington, A. R. Fabris, B. J. Howard and N. J. D. Lucas, "Proceedings of the International Symposium on Electronic and Nuclear Magnetic Resonance", (Melbourne, Australia, 1969).
13. A. Carrington, A. R. Fabris, B. J. Howard and N. J. D. Lucas, Mol. Phys. to be published.
14. C. Bloch, Nuc. Phys. 6, 329 (1958).
15. A. Messiah, "Quantum Mechanics" Chapter 14 (North-Holland Publishing Co., Amsterdam, 1965).
16. H. Marganau and G. M. Murphy, "The Mathematics of Physics and

Chemistry", (Van Nostrand, Princeton, 1956).

17. J. W. C. Johns, J. Mol. Spec. 15, 473 (1965).

18. E. Wigner and E. E. Witmer, Z. Physik. 51, 859 (1928).

19. For example, M. Tinkham, "Group Theory and Quantum Mechanics", (McGraw-Hill, New York, 1964).

## Chapter 9

# Spin-orbit Coupling Constants in Heavy Diatomic Molecules

### 9.1 Introduction

The spin-orbit coupling constants of many of the $^2\Pi$ molecules have been obtained from the second order effects on the g-value of the e.p.r. spectrum. In the J=3/2 level of the $^2\Pi_{3/2}$ state, the effect on the g-value, due to the mixing of the fine-structure states, is obtained from (6.7) and (6.8) as :

$$g_{cor} = -0.800\ Bg_s/A \qquad (9.1)$$

Now the spin-orbit coupling is expected to increase in magnitude on going to heavier molecules. In the halogen oxide series, A increases from -282 $cm^{-1}$ to -815 $cm^{-1}$ on going from ClO [1] to BrO [2]. Then one might expect the value in IO to be about -1500 $cm^{-1}$, but the e.p.r. [2] spectrum suggests a value of -446 $cm^{-1}$. Even allowing for the fact that the spectrum becomes less sensitive to the value of A as its magnitude increases and also considering possible corrections to the g-factor like the rotational Zeeman interaction, there is still a large discrepancy between the expected and 'observed' values of the spin-orbit coupling constant.

In this chapter the value of A for several diatomic radicals is estimated from the values of A for the constituent atoms using a simple L.C.A.O. picture; the hyperfine parameters of the radical and the separate atoms are used to estimate the L.C.A.O. coefficients. These results indicate that for the heavier molecules, the 'observed' values of A should be increased.

In IO, it was pointed out by Dyer et al.[2,3] that if the value of A was increased in magnitude to $-1000$ cm$^{-1}$, the calculated spectrum was moved by 6.2 gauss to higher field. Then, in order to interpret the spectrum, it is necessary to increase the value of the orbital or the spin g-factor. It is suggested that the third order mixing of excited electronic states with larger g-values into the ground state is responsible for this.

## 9.2 Expected Spin-orbit Coupling Constants in $^2\Pi$ Molecules

Dixon and Kroto[4] have suggested that if the orbital containing the unpaired electron in a $^2\Pi$ radical can be written as a linear combination of 2p atomic orbitals,

$$\psi_{XY} = a_X \phi_X + a_Y \phi_Y \qquad (9.2)$$

the spin-orbit coupling constant can be obtained from the spin-orbit coupling constants of the separate atoms, weighted by the unpaired electron density on that atom. That is :

$$|A_{XY}| = a_X^2 |A_X| + a_Y^2 |A_Y| \qquad (9.3)$$

Modulus signs are used because the actual sign of the spin-orbit coupling constant depends upon whether the valence orbitals are more or less than half filled.

Some care must be taken in using the values of A from atoms in states other than $^2P$. Thus the group 3 and group 7 values may be used directly, but the group 4 and 6 atoms have $^3P$ ground states containing two unpaired electrons, both in p-orbitals.

As was pointed out by Blume and Watson [5], the spin-orbit Hamiltonian for the two unpaired electrons can be written approximately in two ways, namely :

$$\mathcal{H}_{so} = A\,\underline{L}.\underline{S} = \sum_i \xi\,\underline{l}_i.\underline{s}_i \tag{9.4}$$

This neglects the spin-other-orbit interaction and assumes that the coefficient $\xi$ is the same for all the unpaired electrons; these are reasonably correct for the two unpaired electrons in a $^3P$ state. Since both of these unpaired electrons are in p orbitals, it is possible (from an evaluation of the matrix elements) to make the substitution :

$$\xi = 2S\,A \,, \tag{9.5}$$

and it is the values of $\xi$, corresponding to a single unpaired p electron, that must be used in (9.3) instead of A. These values of $|\xi|$ for the group 4, 6 and 7 atoms are tabulated below.

$$C = 28\ \text{cm}^{-1}, \quad Si = 150\ \text{cm}^{-1}, \quad Ge = 880\ \text{cm}^{-1},$$

$$O = 147\ \text{cm}^{-1}, \quad S = 374\ \text{cm}^{-1}, \quad Se = 1870\ \text{cm}^{-1},$$

$$F = 269\ \text{cm}^{-1}, \quad Cl = 587\ \text{cm}^{-1}, \quad Br = 2456\ \text{cm}^{-1}, \quad I = 5070\ \text{cm}^{-1} \qquad (9.6)$$

In all the $^2\Pi$ diatomic molecules that have been observed by e.p.r. (except NO, NS and hydrides), one of the atoms is a halogen, so that it is possible to derive the L.C.A.O. coefficients by comparing the hyperfine parameters with those of the atoms.

In $^2\Pi$ radicals, the axial component of the hyperfine interaction, h, is given by :

$$h = g_N \beta \beta_N \left\langle \frac{2}{r^3} \right\rangle_L + \frac{4\pi g}{3} \psi^2(0) + g \left\langle \frac{3\cos^2\theta - 1}{2r^3} \right\rangle_S \qquad (9.7)$$

The corresponding parameter, a', for the hyperfine interaction in $^2P$ atoms is given by approximately 5/8 times the expression above. Then assuming that the hyperfine constant of the halogen atom in the radical is proportional to the unpaired electron density on that atom :

$$a^2_{Hal} = \frac{5h}{8a'} \qquad (9.8)$$

These results are given in column 4 of table 9.1.

It is now possible to calculate the spin-orbit coupling constants in the radicals by assuming :

**Table 9.1** Comparison of the spin orbit coupling constants obtained from the e.p.r. spectra of $^2\Pi$ diatomic molecules with those calculated from the hyperfine parameters using a simple L.C.A.O. picture.

| Radical | h MHz | a' MHz | $a^2_{Hal} = 5h/8a'$ | $\lvert A_{calc}\rvert$ cm$^{-1}$ | $\lvert A_{obs}\rvert$ cm$^{-1}$ |
|---|---|---|---|---|---|
| SF | 428 | 2010 | 0.133 | 360 | 387 |
| SeF | 326 | 2010 | 0.112 | 1706 | 560 |
| CF | 663 | 2010 | 0.206 | 78.5 | 77.1 |
| $Cl^{35}O$ | 111 | 207.4 | 0.342 | 297 | 282 |
| $Cl^{37}O$ | 93 | 174. | | | |
| $Br^{79}O$ | 504.5 | 884.8 | 0.356 | 968 | 815 |
| $Br^{81}O$ | 543.9 | 953.8 | | | |
| IO | 582.1 | 827.3 | 0.440 | 2300 | 446 |

$$a_{Hal}^2 + a_X^2 = 1 , \qquad (9.9)$$

and using the modified form of (9.3) :

$$|A_{XHal}| = a_X^2 |\xi_X| + a_{Hal}^2 |\xi_{Hal}| \qquad (9.10)$$

These calculated values of A are compared with those obtained from the e.p.r. spectrum in columns 5 and 6 of table 9.1.

For the lighter radicals like CF, SF and ClO, the agreement between the two values is fairly good (about ± 5%), giving us hope that this approach is fairly accurate. In BrO, the agreement is slightly worse, while in SeF and IO, the discrepancy is extremely large.

## 9.3 The Effect of Hund's Case (c) Coupling

If we believe the large values of the spin-orbit coupling obtained in the previous section, there will be very large mixing of excited states into the ground wave-function. For a spin-orbit coupling constant of about 1000 $cm^{-1}$ and with an electronic excitation energy of about 20,000 $cm^{-1}$, there may be about a 5% contribution from excited states with $\Delta\Lambda=\pm1$ and $\Delta\Sigma=\mp1$ to the ground state wave-function. Thus, in the new electronic wave-function, $\Lambda$ and $\Sigma$ are no longer conserved, although $\Omega$ is still a fairly good quantum number. This corresponds to Hund's coupling case (c) [6,7]. If the magnetic moment along the axis in the excited state is greater than that in the ground state, it is possible to obtain the necessary correction to the calculated g-factor that will explain the IO spectrum.

All the major effects of the large mixing of electronic states can be obtained by extending the effective Hamiltonian in the ground electronic state (see 5.39) to include the third order terms in the perturbation expansion.

The third order terms have the form :

$$\mathcal{H}^{3}_{\mathrm{eff}} = P_{o}\mathcal{H}'(Q_{o}/a)\mathcal{H}'(Q_{o}/a)\mathcal{H}'P_{o} - P_{o}\mathcal{H}'(Q_{o}/a^{2})\mathcal{H}'P_{o}\mathcal{H}'P_{o} \qquad (9.11)$$

This may appear to be non-Hermitian, but it only gives non-Hermitian contributions if $\mathcal{H}^{3}_{\mathrm{eff}}$ can connect ground states which have different diagonal matrix elements of $\mathcal{H}'$. In such a case, the symmetrised form may be used since the inaccuracies of this manipulation only appear in fifth order.[8]

The only significant third order contributions to the effective Hamiltonian occur when the spin-orbit perturbation is taken twice in (9.11). Also unless it is used in the matrix elements of the form $P_{o}\mathcal{H}'Q_{o}$, the resulting terms in the Hamiltonian mix the widely separated fine structure states and give negligible contributions to the energy. In the e.p.r. spectra, it is likely that the greatest effect is produced if the remaining matrix element contains the

Zeeman perturbation. That is :

$$\mathcal{H}^3_{\mathrm{eff}} = \sum_n \langle \ell_o | \mathcal{H}_{so} | \ell_n \rangle \langle \ell_n | \mathcal{H}_{so} | \ell_o \rangle (E_n - E_o)^{-2} \beta H_z \times \left\{ \langle \ell_n | g_L L_z + g_s S_z | \ell_n \rangle - \langle \ell_o | g_L L_z + g_s S_z | \ell_o \rangle \right\} \tag{9.12}$$

$$= \Delta g \, \beta H_z \, L_z \tag{9.13}$$

The spin orbit coupling can mix in $\Sigma$ and $\Delta$ states with $\Omega = 3/2$, and with multiplicity (2S+1) equal to 2 or 4. The $\Delta$ states yield a negative contribution to $\Delta g$ while the $^4\Sigma_{3/2}$ states give a positive contribution.

## 9.4 Effect on the e.p.r. spectra

As was mentioned earlier, Dyer et al. have pointed out that if the A value of IO is increased to -1000 $\mathrm{cm}^{-1}$, the spectrum is shifted by 6.2 gauss to higher field. If we take the even higher value of A, determined in section 9.2 (i.e. 2300 $\mathrm{cm}^{-1}$), the calculated spectrum will be 9.0 gauss too high. To over come this, we can introduce the correction to the axial magnetic moment, giving $\Delta g = 0.0023$.

In the second rotational level, the effect of A on the spectrum is increased (this effect is proportional to J(J+1)-3/2).

However $\Delta g$ has the same percentage effect on the g-value in all rotational levels. Thus, since $\Delta g$ and A have different effect on the spectrum in different rotational levels, a measurement of the g-value in the $J = 5/2$ as well as the $J = 3/2$ level should permit a separation of the two effects. For example, if $A = -2300\ \text{cm}^{-1}$ and $\Delta g = 0.0023$, the calculated spectrum of IO in the $J = 5/2$ level would appear at about 35 gauss higher field than if $A = -446\ \text{cm}^{-1}$ and $\Delta g = 0.0$ . Preliminary experimental results [9] on the second rotational level of SeF suggest that a larger value of A is needed.

The only well characterised spectrum, in which a $\Delta g$ correction has been introduced, is that of SeH (and SeD).[10,11]. The rotational constants of these two radicals differ by practically a factor of two so that there is considerably different rotational mixings of the fine-structure states. It is thus possible, after removing the high order Zeeman contributions, to attribute the observed difference in the g-values of the two $J = 3/2$ spectra to the term $(B_H - B_D) \times 1.6\ H/A$ (see equations 6.7 and 6.8). One then obtains a definite value of A, which is considerably different and much larger in magnitude than that obtained from each spectrum separately. This leaves a g-value correction, $\Delta g = 0.0007_5$. Work on the second rotational level of SeH has confirmed the necessity for this correction. Lucas et al. have attributed this correction in the g-value to the gauge invariance of the spin-orbit coupling (see expression 3.211 where p should strictly speaking be replaced by $\Pi$). They then use Slater type orbitals to estimate the magnitude of A and $G_0$ (their $G_0$ equals $2\Delta g$). They neglect the shielding effects of the electrons and obtain a value of A that is very close to that obtained from experiment; this is presumably because A has a $1/r^3$ dependence on the distance between particles so that its most important contribution comes from near the nuclei, where shielding will be unimportant. It is unlikely that this approximation is alright for calculating $G_0$ which has only a $r^{-1}$ dependence on the distance between the unpaired electron and the other charges. Although their calculated value of $G_0$ is in fair agreement with experiment, it is almost certainly an order of magnitude too large. It also seems that their correction has the wrong sign to explain the g-value discrepancy. It is proposed that the tendency to case (c) coupling is the true solution.

All the radicals considered here (IO, BrO and SeF) will require a positive value of $\Delta g$ in order for the magnitude of A to be increased; this means that the main mixing must be with $^4\Sigma$ excited states. These radicals all have the same valence configuration, namely $(z\sigma)^2(y\sigma)^2(w\sigma)^2(x\sigma)^2(v\pi)^3$. The first excited states are : .... $(x\sigma)^1(v\pi)^4$ yielding $^2\Sigma$; .... $(x\sigma)^2(v\pi)^2(u\sigma)^1$ yielding $^4\Sigma$, $^2\Sigma$ and $^2\Delta$; .... $(x\sigma)^2(v\pi)^2(u\pi)^1$ yielding $^4\Pi$, $^2\Pi$, $^2\Pi$, and $^2\Phi$.

Thus there is both a $^4\Sigma$ and a $^2\Delta$ state from the same excited configuration. Since they will have approximately the same energy and their spin-orbit coupling matrix elements (in a single configuration approximation) with the ground state are the same, it is difficult to predict the sign of $\Delta g$ a priori.

It is also possible that the case (c) coupling may be needed to explain the anomalies in the spectra of molecules, not in $^2\Pi$ states, but still containing heavy nuclei. For example, in the $^1\Delta$ state of SeO, an extremely large rotational g-factor has to be introduced in order to explain the spectrum[12]; $g_r^e$ was $14 \times 10^{-4}$ while the expected value is about $2\times10^{-4}$. A possible solution is to introduce a positive $\Delta g$, obtained from the mixing in of $^3\Pi_2$ states. The measurement of the second rotational level (J = 3) should again permit us to establish which is the correct solution.

## References to Chapter 9

1. A. Carrington, P. N. Dyer and D. H. Levy, J. Chem. Phys. 47, 1756 (1967).
2. A. Carrington, P. N. Dyer and D. H. Levy, J. Chem. Phys. 52, 309 (1970).
3. P. N. Dyer, Ph.D. Thesis (Cambridge, 1969).
4. R. N. Dixon and H. W. Kroto, Trans. Far. Soc. 59, 1484 (1963).
5. M. Blume and R. Watson, Proc. Roy. Soc. A, 271, 565 (1963).
6. G, Herzberg, "Molecular Spectra and Molecular Structure. 1. Spectra of Diatomic Molecules", (D. Van Nostrand, Princeton, N. J., 1950).
7. F. Hund, Z. Physik. 36, 657 (1926); 40, 742 (1927); 42, 93 (1927).
8. C. E. Solverez, J. Phys. C, 2, 2161 (1969).
9. C. R. Byfleet and D. K. Russell, private communication.
10. A. Carrington and N. J. D. Lucas, Proc. Roy. Soc. 315, 355 (1970).
11. N. J. D. Lucas, Ph.D. Thesis, (Southampton, 1969).
12. G. N. Currie, Ph.D. Thesis (Cambridge, 1968).

Footfalls echo in the memory
Down the passage which we did not take
Towards the door we never opened
Into the rose-garden.

T. S. Eliot:
Four Quartets, 'Burnt Norton',I.