Chapter 8 Nuclear Moments 2: Experimental Measurements

8.1 The determination of nuclear moments from optical spectrometry

8.1.1 Early history of optical spectroscopy

As early as 1924, Pauli suggested that the hyperfine structure which had been observed in optical spectra, and which at the time lacked a satisfactory explanation, could possibly be arising from the effects of a *nuclear* magnetic moment. However, considerable advances in the theoretical understanding of the atomic system and its associated optical spectrum were necessary before this suggestion could be tested experimentally. We proceed briefly to summarize the interpretation of optical spectra with a view to outlining the role that the nuclear electric and magnetic moments play in this field of study so that it may be seen how information concerning the magnitude of these moments is to be obtained from spectral measurements. An understanding of the ideas and concepts of atomic physics is particularly relevant to our study of the nucleus since nuclear physics has borrowed heavily from the established ideas and concepts of atomic physics.

During the nineteenth century, extensive studies were made with optical spectrometers of the line spectra emitted and absorbed by the various chemical elements. Each element was found to have its own characteristic pattern of lines, a fact which was of the greatest practical importance for the identification of the elements in chemical and astronomical applications. The first step towards an understanding of the physical implications of the spectral lines was taken by Balmer in 1885. He found that if, instead of considering wavelength λ , whose measurement was in general the object of the experimental researches, one worked with the wave number k, then the nine known lines in the visible and ultraviolet spectrum of hydrogen were well fitted by the formula

$$k\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{m^2}\right],$$

with $m = 3, 4, 5, \ldots$, etc. with a suitable choice of the value for R, called the Rydberg constant. Now, since $\lambda = c/\nu$, its reciprocal k is proportional to the frequency ν . The reason for the success of Balmer's empirical formula became clear with the introduction of the quantum concept. On the quantum view the energy is emitted in the form of photons, each photon having an energy content

given by $h\nu$. Thus the energy of the photon is proportional to k. Balmer's formula can then be interpreted as expressing the photon energy as the difference between a fixed energy and a set of discrete energy values. This led to the picture of the atom having a series of excited states, each of well-defined energy, the energies of these states forming the *terms* in the Balmer formula and the emitted photon carrying off the excess energy when a transition from a higher to a lower energy state occurs. On this view absorption finds an explanation in the transition from lower to higher energy states. A knowledge of the wavelengths of the optical spectral lines thus enables us to find very accurately the difference in energy content of the various excited states of the atom.

Bohr in 1913 introduced the assumption that in hydrogen stationary (i.e. non-radiating) states correspond to circular orbits of the electron of radius such that the angular momentum is $n\hbar$, where n is an integer. This led to energy values which corresponded with precision to the terms in Balmer's formula. n was referred to as the quantum number; its value determined the energy of the state.

8.1.2 Fine structure

When it became possible to examine the Balmer lines with higher resolution it was discovered that they were not in fact single but consisted of groups of lines called *multiplets*. Whereas the spacings between the lines given by the Balmer formula was of the order of tens of nanometres, the spacing between the members of a multiplet was of the order of hundredths of nanometres. This difference represents the justification for referring to the multiplets as constituting *fine structure*. Sommerfeld (1915) sought to explain fine structure by introducing elliptic orbits requiring a second quantum number n_{θ} for their description. In the non-relativistic approximation, and in the Coulomb field, the energy corresponding to an orbit is independent of n_{θ} for the orbit, being the same for the whole set of ellipses (including the circle), with the same value of n, which now became known as the *principal* quantum number. This degeneracy is removed when the relativistic mass dependence on velocity is introduced or when the field differs significantly from the Coulomb field; the energy of the system then depends slightly on n_{θ} .

These quantum-based ideas, developed to explain the single-electron hydrogen atom, had also a limited success when applied to the more complicated atoms of the alkali elements. In so far as the electronic configuration of these elements consisted of one electron orbiting outside one or more closed shells of electrons, the optical activity associated with this electron was expected to show hydrogenlike behaviour. However the field of the nucleus with its charge Ze screened by the Z - 1 electrons in the closed shells is not precisely Coulombic, even beyond the outer shell. Moreover, electrons on certain elliptic orbits would be expected to penetrate the shells. Thus the fine structure is expected to be more marked. Despite the complications certain progress was made in interpreting series of lines observed in terms of atomic energy levels. The Sommerfeld interpretation of fine structure was not however entirely satisfactory and in 1925 Goudsmit and Uhlenbeck proposed the idea of electron spin to justify the introduction of a further quantum number. This proposal also had the merit of resolving certain difficulties which at that time existed in interpreting the results of atomic-beam experiments.

In 1928 the theory was put on a much more satisfactory basis with Dirac's formulation of a relativistic wave equation for the electron, in which electron spin found a natural role. Dirac's theory led to a formula for fine structure in which there was a contribution from electron spin and also a contribution from the relativistic mass effect.

It is not however usually necessary to introduce the complications involved by having recourse to the Dirac formula. For many purposes it is sufficient to use the non-relativistic Schrödinger equation for a point electron in a field whose potential is appropriate to the atom under consideration, and to make separate allowance for the energy of interaction of the magnetic moment of the electron with the magnetic field arising from the relative motion of electron and charged nucleus. This interaction is the so-called *spin-orbit interaction*.

The solution of Schrödinger's equation then involves, as in the analysis of section 6.3, quantum numbers n, l, m, the eigenvalues being, as in the Bohr treatment, degenerate with respect to l and m. This degeneracy is removed when the field is not strictly Coulombic or when allowance is made for the relativistic mass effect. The introduction of electron spin s leads to the modification of the quantum numbers. These, in the presence of spin-orbit coupling, now become n, l, j, m_j , where $j = l \pm s$ and m_j is the projection of j on a specified axis.

The probability of transitions occurring between two particular states, which governs the intensity of the associated spectral line, is strongly dependent on the quantum numbers associated with the initial and final states. The transitions are most likely, and hence lead to observable line intensities, when certain *selection rules* are obeyed. For this reason it is very important to be able to label states of the atomic system with the appropriate quantum numbers.

In the case of one-electron atoms (e.g. hydrogen, singly ionized helium) the quantum numbers to be associated with the states are those of the single electron. In the case of the alkali elements, the optical activity is mostly associated with the valence electron. The closed shells having zero total orbital angular momentum and zero total intrinsic electron spin, the atomic states again can be satisfactorily labelled with the quantum numbers of the single valence electron.

In the case of other atoms where more than one electron is involved outside a closed shell, the quantum numbers of the atomic state have to be constructed from those of the electrons involved. Normally this is carried through by combining vectorially the individual orbital angular momenta to form a resultant orbital angular momentum L and the spin angular momenta to form a combined spin angular momentum S. A total angular momentum J is then formed by combining L and S vectorially. Associated with the quantum number J is the magnetic quantum number M arising from the projection of J on a specified axis. The selection rule which is found normally to operate is that, between initial and final atomic states, $\Delta J = \pm 1$ or 0, with the usual proviso that a transition from a state with J = 0 to a second state with J = 0 is forbidden. It is usual for there to be no change in S so that $\Delta L = \pm 1$ or 0.

Analogous with the energy dependence on orientation of a magnetic dipole in a magnetic field in classical physics, there is a dependence of the atomic energy on the orientation of S with respect to L. Thus we can have states with the same values of L and S, but different J-values, which differ from each other slightly in energy content.

As an example of the application of these ideas let us consider the neutral atom of mercury. We consider its complement of eighty electrons to be arranged as follows. The first five shells are complete, i.e. mercury has a core of similar electronic configuration to the atom of xenon (Z = 54). In the sixth shell there are complete subshells corresponding to fourteen electrons with n = 4, l = 3, together with all the possible values of j and m_i , ten electrons with n = 5, l = 2and two electrons with n = 6, l = 0. We can now consider excited states of the atom in which one of the latter two s-electrons is displaced into an orbit of higher energy, this being the sole change in the configuration. The electrons in the completed shells and subshells have zero total angular momentum and zero total spin. Hence to find L and S we need only consider the last two electrons. Of these, the undisturbed member of the pair has l = 0. Thus the value of L will be equal to the *l*-value of the disturbed electron, while S may be 1 or 0 depending on the parallelism or antiparallelism of the electron spins. By promoting this single electron to an orbit with L = 1 the ground-state configuration, which we denote by S_0 (the conventional symbol for L = 0, J = 0), is changed into one of the following three configurations:

 P_0 (L = 1, J = 0, arising from S = 1, L and S antiparallel),

 P_1 (L = 1, J = 1, arising from S = 1, L and S at 120°) and

 P_2 (L = 1, J = 2, arising from S = 1, L and S parallel).

Similar considerations show that if the second electron is raised into an orbit with l = 2 we can then have configurations:

 $D_1 (L = 2, J = 1, S = 1),$ $D_2 (L = 2, J = 2, S = 1)$ and $D_3 (L = 2, J = 3, S = 1).$

These groups of P- and D-states are said to constitute *triplets*, each having a *multiplicity* of three. Transitions between the components of the D-triplet and the components of the P-triplet take place, the probabilities of these transitions being governed by the selection rules stated above. In Figure 37 the levels corresponding to these states are illustrated and the wavelengths of the emitted quanta indicated to show the wavelength differences involved in the structure arising from the spin-orbit interaction.





8.1.3 Hyperfine structure

When the developments of spectroscopy made it possible to observe with still higher resolution, structure even finer than the fine structure we discussed above was discovered. For example a 'line' of wavelength 359.6 nm in the spectrum of bismuth was found to contain six components within a wavelength range of 0.03 nm (equivalent to a range of wave numbers of 230 m^{-1}). Structure of this order of fineness is referred to as hyperfine structure.

In some cases hyperfine structure is due to the existence in the sample of more than one stable isotope of the element being investigated. When the sample consists of an isotopic mixture, there appear to be two distinct reasons for slight differences occurring in the spectral lines emitted by the different isotopes, in spite of the fact that they must be assumed to have identical electron configurations. Firstly, the different nuclear masses of the isotopes lead to different reduced masses (see section 3.6) for the nucleus-electron system. The different reduced masses reflect the different relationships between the centre-of-mass and laboratory coordinate systems, and slightly affect the energy. The differences between the spectrum of hydrogen (Z = 1, A = 1) and deuterium (Z = 1, A = 2) is well explained on this basis. In fact this was a central consideration in the argument made by Urey in 1932 for the existence of a heavy isotope of hydrogen. However, in the case of the heavier elements this explanation is not satisfactory and the isotope shift may in fact be in the opposite direction to that

predicted by making allowance for the change in reduced mass. In these cases the dominant cause is believed to be a dependence of the nuclear radius, and consequently of the Coulomb field close to the nucleus, on the number of neutrons in the nucleus.

However, hyperfine structure is not solely isotope structure. This became clear when hyperfine structure was discovered in an element like bismuth which is known to be mono-isotopic. Thus a further explanation for hyperfine structure had to be sought. We recollect that in the case of fine structure the introduction of a new quantum number s, the electron spin, and of a new interaction, namely spin-orbit interaction, provided a satisfactory theoretical basis for its discussion. So in the case of hyperfine structure we resort to the same expedients. We recall Pauli's suggestion concerning the nuclear moments and we take the new quantum number to be I, the nuclear spin. The new interaction to be considered is the interaction between the magnetic and electric moments of the nucleus, which are related to its spin and its charge distribution, and the electric and magnetic field at the site of the nucleus due to the orbital atomic electrons.

Just as we combined L and S to form J, so we now combine J and I to form F which will be taken to represent the angular momentum of the whole atom, including the contribution from the intrinsic nuclear spin. Again, analogous to the previous case, the energy of the system depends slightly on the orientation of I with respect to J. Thus states with the same J and I quantum numbers but differing in F quantum number can have slightly different energies. We note that F can take the values J + I, J + I - 1, J + I - 2, ..., |J - I|, giving 2J + 1 different values providing $J \leq I$, and 2I + 1 different values if $J \geq I$.

Assuming J to be known from the interpretation of fine structure, then the number of hyperfine structure components associated with the various states provides important information about the value of I. If J = 0, there is of course only one possible value of F, irrespective of the value of I, and hence all states with J = 0 are expected to be singlets. If $I = \frac{1}{2}$ then, apart from states with J = 0. all states will have two hyperfine components. If $I > \frac{1}{2}$ then there will be 2J + 1or 2I + 1 components, depending on whether $J \leq I$ or J > I. Transitions between components of two hypermultiplets will of course be governed by a selection rule which is found to be $\Delta F = \pm 1$ or 0, with $F = 0 \rightarrow F = 0$ forbidden. We now take the particular example of a hypermultiplet namely that of the 377.7 nm $(k = 2647.8 \text{ mm}^{-1})$ line in thallium. This is believed to be a P₁ \rightarrow S₁ transition. If we tentatively assign a value of $\frac{1}{2}$ to the spin of the thallium nucleus, then in the case of the upper-state J-value being $\frac{1}{2}$, we can have F = 1 or F = 0. Again, J being $\frac{1}{2}$ for the lower state, F can be 1 or 0 for this state. The energy levels and transitions are illustrated in Figure 38 and these provide a satisfactory explanation for the pattern of lines observed.



Figure 38 Interpretation of fine structure and hyperfine structure in the optical spectrum of thallium

Consider the further more complicated example arising in the case of singly ionized praseodymium. The J-values of the states are believed to be large. We take them to be 7 and 8, although the argument is unaffected providing they are greater than I, which we tentatively take to be $\frac{5}{2}$. Then as illustrated in Figure 39 each state has 2I + 1, i.e. six, components. The above selection rule then predicts the line pattern shown and this is in good agreement with observations. Thus the assignment of the value $\frac{5}{2}$ to I is confirmed. Any other value of I (subject always to J > I) can be shown to predict a different appearance for the hypermultiplet.

We thus have, always providing some information is available concerning the J-values, a very powerful method for determining J from the line pattern alone. We now turn to the other information available which we have not so far used, namely the spacing between the lines in the spectrum. This spacing is of course related to the spacing between the energy levels and in turn this is related to the interaction energy associated with the orientation of the nucleus.



Figure 39 Interpretation of hyperfine structure of an optical line in the spectrum of Pr⁺

8.1.4 The determination of nuclear magnetic moments

Consider first the effect of the nuclear magnetic moment. As discussed in section 7.3, this quantity is related to the spin angular momentum and we take the magnetic moment to be $\mu_{\rm I}$ parallel to I, the absolute angular momentum. We note that $\mu_{\rm I}$, like I, is not observable and that the maximum observable time-averaged magnetic moment is given by

$$\mu_I = \mu_1 \frac{I}{\sqrt{[I(I+1)]}}$$

This effective magnetic moment will interact with the magnetic field produced at the nucleus by the orbital atomic electrons. We assume this field to be H_J , antiparallel to J. (The antiparallelism is taken because the negative charge of the electron leads to this relative orientation for a single-electron atom. The quantities may of course be parallel for multi-electron atoms.) Since the vector J must always precess about a specified direction, the effective magnetic field will always be less than H_J . We denote the effective magnetic field by H_J , where



Figure 40 Vector diagram of coupling of L, S and I

$$H_J = H_J \frac{J}{\sqrt{[J(J+1)]}}$$

We assume that the vectors I and J couple together to form a resultant vector F as shown in Figure 40. The contribution to the total energy of the system arising from the interaction of the nuclear magnetic dipole moment with the atomic magnetic field is then

$$W_{\rm D} = \mu_{\rm I} H_{\rm J} \cos{({\rm I},{\rm J})}.$$

Now from Figure 40 we see that

$$\cos(\mathbf{I}, \mathbf{J}) = \frac{|\mathbf{F}|^2 + |\mathbf{J}|^2 - |\mathbf{I}|^2}{2|\mathbf{I}||\mathbf{J}|}.$$

Hence $W_{\mathbf{D}} = \mu_I H_J \frac{F(F+1) - J(J+1) - I(I+1)}{2|\mathbf{J}|}.$ 8.1

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It is customary to write this expression as

$$W_{\rm D} = \frac{AC}{2},$$

where
$$A = \frac{\mu_I H_J}{IJ}$$
 and $C = F(F+1) - J(J+1) - I(I+1)$.

We now take I and J as fixed quantities and consider F as a variable quantity subject to the condition that its allowed values are I + J, I + J - 1, ..., |I - J|.





Figure 41 Interval rule for magnetic-dipole interaction. μ_l is taken to have a positive value and H_J is assumed antiparallel to J. Note intervals 4A, 3A, 2A proportional to upper F-value

If A is positive, then the higher the value of F the greater the energy associated with the state. By substituting into equation 8.1 we see that the energy difference between a state having a quantum number F and one having a quantum number F-1 will be AF. This constitutes the interval rule for the magnetic dipole interaction. Figure 41 shows the intervals involved in the case where $J = \frac{5}{2}$, $I = \frac{3}{2}$, μ_I is positive and H_J is antiparallel to J.

In the same diagram the displacement of each component with respect to a base line corresponding to $W_D = 0$ is shown. These displacements are given by $\frac{1}{2}AC$ for the different F-values. We note that if, corresponding to the possible orientations for each F-value with respect to a specified spatial direction, a statistical weight 2F + 1 is assigned, and the 'centroid' of the multiplet calculated from

$\sum (2F+1)(W_{\rm D})_F$

then the energy corresponding to the centroid is found to be $W_D = 0$. This means that the multiplet components have a centroid corresponding to the level as it would be determined in an experiment with insufficient resolution to separate the components.

8.1.5 The determination of nuclear electric quadrupole moments

We now consider the interaction between the electric quadrupole moment of the nucleus and the gradient of the electric field at the nucleus. The integration energy is the scalar product of two tensors of degree two, namely the quadrupole moment and the field gradient. This is to be compared with the case of the magnetic dipole interaction, in which the tensors were of degree one, i.e. were

133 The determination of nuclear moments from optical spectrometry vector quantities. The detailed calculation of the quadrupole interaction is beyond the scope of this book and we content ourselves with quoting the results, namely that

$$W_Q = \frac{B}{4} \left[\frac{\frac{3}{4}C(C+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \right],$$

where as before C = F(F + 1) - J(J + 1) - I(I + 1),

and
$$B = eQ \frac{\partial^2 \phi(0)}{\partial z^2}$$
.

If W_Q is comparable in magnitude to W_D there will arise significant deviations from the magnetic dipole interval rule derived in section 8.1.4. This can be seen by considering the case of the hyperfine multiplet corresponding to $J = \frac{1}{2}$, $I = \frac{3}{2}$ illustrated in Figure 42.



Figure 42 Effect of finite quadrupole moment on the hyperfine structure levels. Full lines are for B > 0, dotted lines for B < 0

The first evidence of the existence of a nuclear electric quadrupole moment consisted of these measurable deviations from the magnetic dipole interval rule.

8.2 Limitations to the accuracy of optical determinations of nuclear moments

Accurate optical measurements of hyperfine splitting in conjunction with the above theoretical interpretation enables values of A and B to be determined in many cases. In order to derive μ and Q from these quantities, however, one requires the values of magnetic field gradient and electric field gradient at the nucleus. These fields have to be calculated from the quantum mechanics of the electron orbitals. Apart from the most elementary cases, the accuracy of the calculated values, particularly those of electric field gradients, are open to some doubt. However, to give an impression of the values of fields involved, we quote the result of the calculations for caesium. This atom has one electron in excess of the configuration of xenon. In the ground state the valuece electron is in an

s-state. While it has no orbital angular momentum, nevertheless by virtue of its intrinsic magnetic moment of one magneton, it produces at the nucleus a magnetic field of $2\cdot 1 \times 10^6$ G. We note that an electron at a distance of 10^{-10} m produces a magnetic field of approximately 10^4 G; hence the effectiveness of the s-electron is due to its greater proximity to the nucleus. In fact it produces a greater magnetic field than an electron in a p-orbit, and it is calculated that the value of H(0) for the ground state is about ten times that for the excited states corresponding to p-electrons. The s-electron in the ground state has spherically symmetric charge distribution and does not therefore give rise to an electric field gradient at the nucleus. If however we take the excited states, then the lowest-energy p-electron gives rise to an electric field gradient $\partial^2 \phi(0)/\partial z^2$ of $1\cdot 1 \times 10^{22}$ V m⁻². Note that a charge distribution equivalent to one electronic charge at a distance of 10^{-10} m from the nucleus would produce a gradient of 2×10^{21} V m⁻².

We therefore see that, in principle, values of μ and Q can be obtained from the measured values of A and B using the calculated field values. In the case of the magnetic moments the results are in fairly good agreement with results obtained by other methods, to be described below. However in the case of the electric quadrupole moments the situation is much less satisfactory. This is so for two reasons. Firstly because the interaction energy itself is smaller and secondly because there is more doubt about the effective field gradient at the nucleus than there is about the magnetic field.

Where information concerning the hyperfine splitting is available for two isotopes of the same element, then the ratio of the μ -values or Q-values is much more reliable because the ratio does not depend on the field at the nucleus, which is assumed to be the same for the same electron configurations. From the ratios one can learn how the nuclear magnetic moments are being affected by the addition of neutrons to a particular nucleus. However, even in the case of isotopes there is the possibility that the electron orbitals may be affected by the nuclear quadrupole moment and might therefore not be the same for both isotopes.

The investigation of hyperfine structure calls for the highest available resolution because the very small energy difference between two components of a multiplet is being measured as the difference between two quanta each of very much higher energy. There are now available techniques whereby transitions between components in the multiplet may be directly investigated and as a consequence much greater accuracy can be achieved by these newer methods in the measurement of A and B. These newer techniques in general involve applying an external magnetic field to the atomic system. We now proceed to consider the consequences of the application of such an external field.

8.3 Behaviour of atomic system in a magnetic field

We recall that the system consists of a set of orbital electrons having a resultant angular momentum J. The electrons will also in general have a resultant magnetic moment μ_J taken antiparallel to J and of magnitude of the order of

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the Bohr magneton $(9.2731 \times 10^{-28} \text{ J G}^{-1})$. At the centre of the system we have a nucleus of angular momentum I and magnetic moment μ_{I} parallel to I of magnitude of the order of a nuclear magneton $(5.05038 \times 10^{-31} \text{ J G}^{-1})$. We have already discussed how J and I couple to form a resultant F (see Figure 40, p. 132).

If now this system is immersed in a weak external magnetic field H, F will precess round H, the angle of the cone on which it lies being such that the angular momentum parallel to H is $M_F \hbar$, M_F as usual being integral or zero and $|M_F| \le F$. From the vector diagram of Figure 40 it can be seen that the timeaveraged value of magnetic moment parallel to F, which we denote by μ_F , will be given by

$$\mu_{\mathbf{F}} = \mu_{\mathbf{I}} \cos(\mathbf{I}, \mathbf{F}) - \mu_{\mathbf{J}} \cos(\mathbf{F}, \mathbf{J}).$$

Thus $\mu_{\mathbf{F}} = \mu_{\mathbf{I}} \left[\frac{|\mathbf{F}|^2 + |\mathbf{I}|^2 - |\mathbf{J}|^2}{2|\mathbf{I}| |\mathbf{F}|} \right] - \mu_{\mathbf{J}} \left[\frac{|\mathbf{F}|^2 + |\mathbf{J}|^2 - |\mathbf{I}|^2}{2|\mathbf{F}| |\mathbf{J}|} \right].$

The interaction energy of the resultant magnetic dipole moment of the atomic system with the external field will be given by

$$W_{H} = -\mu_{F} H \cos(F, H) = -\mu_{F} H \frac{M_{F} \hbar}{|F|}$$
$$= -\frac{M_{F} \hbar H}{2|F|^{2}} \frac{\mu_{I}}{|I|} \left[(|F|^{2} + |I|^{2} - |J|^{2}) - \frac{\mu_{J}}{|J|} (|F|^{2} + |J|^{2} - |I|^{2}) \right].$$

This energy increment has to be added to the natural hyperfine energy $\frac{1}{2}AC$ of section 8.1.4.

We now illustrate these general results by considering a particular case. Take $J = \frac{1}{2}$, $I = \frac{3}{2}$; then F = 2 or 1. Taking F = 2 and neglecting μ_1 compared to μ_3 , we have

$$(W_H)_{F-2} = \frac{M_F \hbar H}{4} \frac{\mu_J}{|J|}, \qquad M_F = 2, 1, 0, -1, -2.$$

For F = 1 we have

$$(W_H)_{F-1} = \frac{M_F \hbar H}{4} \frac{\mu_J}{|J|}, \quad M_F = 1, 0, -1$$

In Figure 43 is illustrated schematically the variation of energy as the external field H increases in value.

As H increases, the angular velocity of precession of F about H increases until the simple vector picture ceases to be valid. At very high field strengths F is precessing as fast about H as I and J are precessing about F. When this stage is



Figure 43 Variation of energy of atomic system as the externally applied field H is increased

reached J and I become decoupled and each then precesses independently about H with magnetic quantum numbers M_J and M_T . We then have W_H given by

$$\frac{\mu_J M_J \hbar}{|\mathbf{J}|} H,$$

together with a term

$$\frac{\mu_{\mathbf{I}} M_{I} \hbar}{|\mathbf{I}|} H,$$

which we neglect. However, since the field at the nucleus arising from the orbital electrons is large compared to the external field, we have to allow for the interaction of the nuclear dipole moment with this internal field. The angle between I and J is not now constant as it was in the discussion in section 8.1.4. However the precession of J is fast enough now for us to assume that the effective field at the nucleus is

$$H_{\mathbf{J}}\frac{M_{\mathbf{J}}\hbar}{|\mathbf{J}|},$$

parallel to the direction of the external field *H*. We note that $H_{\mathbf{x}}$ will be antiparallel to $M_{\mathbf{x}}h$. The interaction energy of $\mu_{\mathbf{x}}$ with this atomic field will then be given by

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$$\mu_{\mathbf{I}}H_{\mathbf{J}}\left[\frac{M_{J}\hbar}{|\mathbf{J}|}\right]\left[\frac{M_{I}\hbar}{|\mathbf{I}|}\right] = \frac{\mu_{I}H_{J}}{IJ}M_{I}M_{J}.$$

Thus to W_H , the energy of the magnetic dipole moment of the atomic electrons in the external field, we have to add $AM_I M_J$, the energy of the nuclear magnetic dipole moment in the magnetic field produced at the nucleus by the atomic electrons. In high magnetic fields the first of these two terms is proportional to H and independent of M_I , whereas the second is independent of H but depends on the value of M_I . Thus as H increases, the total energy increases linearly with the different values of M_J , displacing the line for different magnetic substates. This is shown on the right of Figure 43. We now have considered the variation of energy with H in low fields and in very high fields. The discussion of the variation in intermediate fields, when I and J are not completely decoupled, is of a difficulty beyond the scope of this book. We show in Figure 43 the results for intermediate fields and note that the energy varies continuously from the low-field to the high-field values for each state.

We turn from the question of the total energy of the system to discuss the magnetic moment. Conventionally the magnetic moment of the atom is the maximum observed value of the component of magnetic moment parallel to an external field H. The system will be in this state for one set only of the magnetic quantum numbers. We now wish to discuss the magnetic moment of the system for any set of magnetic quantum numbers and find it convenient to introduce the term *effective magnetic moment*, denoted by μ_{eff} , for the component of magnetic moment of the system can then be written

 $W_H = -\mu_{eff} H + a \text{ constant independent of } H.$

It follows that

$$\mu_{eff} = -\frac{\partial W_H}{\partial H}$$



Figure 44 Variation of $\mu_{eff} = -\partial W_H / \partial H$, with increasing H for the system of Figure 43

We can thus derive μ_{eff} from the gradient of the curves in Figure 43. In low fields these values can be confirmed by taking the components parallel to H of $\mu_{\rm F}$ as given by equation 8.2. For high fields

$$\mu_{eff} = -\frac{M_J \hbar}{|\mathbf{J}|} \mu_{\mathbf{J}}, \qquad M_J = \pm \frac{1}{2},$$

assuming the component of μ_{I} to be negligible. In Figure 44 μ_{eff} is plotted. It is to be noted that μ_{eff} is zero not only in the obvious case of low fields with $M_{F} = 0$ but also in intermediate fields for certain other magnetic substates.

It is very important to note that the nucleus influences the behaviour of the atom, not only through its contribution to the energy of the system by virtue of the interaction of its dipole moment with the internal magnetic field, but also through the large contribution which its angular momentum makes to the total angular moment of the system. This is so despite the fact that its magnetic moment is three orders of magnitude smaller than the atomic magnetic moment.

8.4 Behaviour of atomic system in inhomogeneous magnetic field

A basic feature of the atomic-beam experiments which we wish to review is the use of inhomogeneous fields to deflect the beam. We proceed to discuss this deflection in relation to the effective magnetic moment of the atom and to the gradient of the external magnetic field.

Consider the simple case of a classical magnetic dipole, moment μ , lying with the moment parallel to a magnetic field H along the z-axis. If the field H is homogeneous there is no net force acting on the dipole. If, however, the field is inhomogeneous and there is a finite gradient at the origin denoted by $\partial H(0)/\partial z$, then from elementary magnetism we know that there is a resultant force

$$\mu \frac{\partial H(0)}{\partial r}$$

acting along the z-axis. The potential energy of the system with the dipole in the given orientation we can denote by $W_H = -\mu H$, measured with respect to a standard position with the dipole perpendicular to the z-axis. In this magnetic context W_H plays the role that electrostatic potential plays in an electrostatic field and just as the electric field strength is given by the negative gradient of the potential, so the force on the magnetic dipole is given by $-\partial W_H/\partial z$. But

$$\frac{\partial W_H}{\partial z} = -\frac{\partial W_H}{\partial H} \cdot \frac{\partial H}{\partial z} = \mu \frac{\partial H}{\partial z},$$

confirming the result which is otherwise obvious in the elementary case. For a more complicated system the deflecting force is still equal to

$$\frac{\partial W_H}{\partial z} = -\frac{\partial W_H}{\partial H} \cdot \frac{\partial H}{\partial z} = \mu_{eff} \frac{\partial H}{\partial z}.$$

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8.5 Measurement of nuclear spin and nuclear, magnetic and electric moments

The techniques, other than optical spectroscopy, which provide information concerning nuclear spin and magnetic moments can be said in general to fall into two groups; those employing atomic or molecular beams, in which there is no communication of energy between the participating atoms or molecules, and those involving liquid or solid samples where energy can pass from one atom or one molecule in the system to others in the sample.

8.5.1 Beam-deflection measurements of nuclear dipole moments

These measurements involve sending the beam of atoms or molecules along, let us say, the x-direction through an evacuated region in which there is a magnetic field at right angles, say in the z-direction, as in Figure 45. This field, which we denote by H_z , is designed to have a high value of the gradient $\partial H_z/\partial z$. Such a field can be achieved by the use of two electrical conductors carrying oppositely directed electric current. If no ferromagnetic materials are used then H_z and $\partial H_z/\partial z$ can be calculated with accuracy. If, however, higher field values are required these can be achieved from practical current densities by introducing ferromagnetic poles shaped to follow the magnetic equipotentials. In this case the field gradients have to be measured because of uncertainty about the behaviour of the ferromagnetic material and considerable practical difficulties may be entailed.



Figure 45 Trajectory of particle with magnetic moment through a magnetic field of constant gradient

Let us now consider classically the trajectory through such a field of an atomic system which has angular momentum I and magnetic moment μ_I parallel to the spin axis. If the dipole axis lies at an angle θ to the field direction then it will experience a couple of moment $H_x \mu_I \sin \theta$ about an axis normal to the plane containing H_x and μ_I . The existence of angular momentum however ensures that this couple does not simply align μ_I and H_z . The necessary increase of angular momentum created by the couple is achieved by rotation of the (H_x, μ_I) plane about the z-axis. The angular velocity of this rotation, called the *Larmor precession*, we denote by ω_L . It follows from the laws of classical dynamics that the rate of increase of angular momentum, $|I|\omega_L \sin \theta$, is equal to the moment of the applied couple, $\mu_I H_x \sin \theta$. Hence

 $\omega_{\rm L} = \frac{\mu_{\rm I}}{|{\rm T}|} H_z.$

It is important to note that ω_L is independent of θ , the orientation of the dipole with respect to the field.

The dipole experiences, in addition to the couple, a net translational force in the z-direction, as discussed in section 8.4. In this case the net force is

$$\frac{\partial H_z}{\partial z}$$

in the z-direction. (The gradient $\partial H_z/\partial z$ must, from the field equations for a static field, be associated with a gradient in the x- and/or y-directions. Strictly speaking there should therefore be one or more additional terms in the expression for the force. However, any such additional terms reverse in direction as the dipole precesses and their total effect is averaged out over one cycle of the Larmor precession.) The acceleration f along the z-direction will then be given by

$$\frac{1}{M} \frac{\cos \theta}{\partial z} \frac{\partial H_z}{\partial z}.$$

If the atom enters the system on the x-axis with a velocity v_0 and at an angle ϕ to the x-axis, and travels a distance L through the field, then it will spend a time $L/v_0 \cos \phi$ in the field and, from elementary kinematics, may be shown to travel a distance

$$= L \tan \phi + \frac{1}{2} \frac{fL^2}{v_0^2 \cos^2 \phi}$$

from the x-axis before it leaves the field. We can alternatively express the deflection as

$$s = L \tan \phi + \frac{1}{4} \frac{\mu_{\rm I}(\cos \theta) L^2}{T \cos^2 \phi} \frac{\partial H_z}{\partial z},$$

where T is the kinetic energy of the atom as it enters the field.

It is interesting to calculate the deflection that can be expected in a practical situation. With $\partial H_z/\partial z = 10^7$ G m⁻¹, $T = 1.4 \times 10^{-20}$ J (which corresponds to the atoms being in thermal equilibrium at 1000 K), $\mu_{\rm I} \cos \theta$ of the order of a Bohr magneton (9 × 10⁻²⁸ J G⁻¹) and L = 0.5 m, an atom entering along the axis will be deflected 45 mm. If, on the other hand, the magnetic dipole moment were of the order of nuclear rather than Bohr magnetons, then the deflection would be about 2.5 × 10⁻² mm.

The first experiments involving this technique were those of Stern and Gerlach (1922) which first established spatial quantization and played an important historical role in the development of quantum theory. In the Stern and Gerlach experiments a beam of silver atoms was used and it was discovered that the deflected atoms fell into two separated groups. This was interpreted as arising from the spatial quantization of atomic dipoles, which were capable of having only two magnetic quantum numbers. This meant that J had to be equal

to 1. A certain spread about the discrete s-values is to be expected because of the variation of v_0 in the beam emitted from the oven which acted as the source of neutral silver atoms. In an experiment of this kind, should the nucleus have spin and magnetic moment, then in principle this should alter the observed deflection. The values of H_z normally used are strong enough completely to decouple J and I and consequently, as discussed in section 8.3, the magnetic moment is only altered by an amount of the order of a nuclear magneton. From the numerical example cited above it is clear that the associated change in deflection could not be detected because of the effect of the velocity variation in the atoms in the beam. If however the nucleus had spin 3, then at some reduced field the effective atomic dipole moment, again as discussed in section 8.3, should vanish and there should be no deflection of the atom. Thus a collimator defining a very small solid angle with respect to the beam source, set up beyond the deflecting magnet, will transmit a beam which, as H_z is decreased from high values, will at some critical intermediate value show a marked rise in intensity. This effect is the more marked since the effective dipole moment vanishes at the same H, value for atoms of all velocities. Quantum theory has then to be invoked to relate the critical field to the nuclear moment. This method of measuring nuclear magnetic dipole moments is known as the zero-moment technique.

In another application a beam of molecules, having no magnetic moment arising from the orbital electrons, is used. If in this case any deflection is observed then it must be due either to the nuclear moment, to a moment associated with rotation of the molecule or to diatomic moments induced in the electron system by the applied field. All of these moments can be of the same order and the separation of the effects is extremely complicated. Nevertheless it was possible by this method (Frisch and Stern, 1933) to make the first measurement of the proton magnetic moment using a beam of hydrogen molecules.

8.5.2 Magnetic resonance beam methods

A new order of accuracy in the measurement of nuclear magnetic dipole moments became possible with the application by Rabi and his associates (in 1939) of



Figure 46 Schematic representation of atomic-beam resonance experiment. The resonant disturbance of the beam is arranged to take place in magnet C in which there is no gradient of magnetic field

resonance techniques to atomic and molecular beams. Schematically the apparatus is shown in Figure 46. The magnet A is a deflecting magnet of the inhomogeneous type described in section 8.5.1. Magnet B is a second inhomogeneous magnet arranged to have H_{τ} in the same direction but the gradient $\partial H_z/\partial z$ reversed as compared to A. C is a magnet with a uniform field H_c . When $H_{\rm C}$ is zero, magnet B can be adjusted to compensate for the effect of magnet A and to bring the original beam on to the detector situated on the axis of the apparatus. This restoration of the beam by the magnet B is independent of the velocity of the atoms or molecules in the beam. When the field $H_{\rm C}$ is increased from zero the particles in the beam by virtue of their magnetic dipole moment will have a Larmor precession but will undergo no deflection because magnet C has a homogeneous field. The compensating effect of B is dependent on the atom or molecule maintaining its original magnetic state, i.e. the orientation θ has to be the same in B as it was in A. The Larmor precession in the magnet C does not of itself change the magnetic state of the atom or molecule. If, however, we arrange for a magnetic field H_0 to be applied perpendicular to H_0 , and to rotate about H_{C} , there will be a tendency for precession to take place about H_0 as well as about H_C . This means that there will be a tendency for the orientation θ to alter. If H_0 rotates with an angular velocity different from that of the Larmor precession then the disturbance to θ will be sometimes tending to increase its value, at other times tending to reduce it. The net effect will average to zero. Should, however, H_0 rotate with an angular velocity exactly equal to the Larmor angular velocity then there will be a disturbance which will act steadily to alter θ in one direction. The simplest way to achieve a rotating magnetic field is to feed high-frequency electric current to a fixed coil having its plane arranged to contain the direction of the magnetic field $H_{\rm C}$. This will produce a field H sin ωt in a fixed direction perpendicular to H_C. Formally this is equivalent to the superposition of two fields, each of strength $\frac{1}{2}H$, rotating in opposite senses with angular velocity ω in a plane perpendicular to H_C . If $\omega = \omega_L$, one of these fields will produce on average no effect on the precessing system, as it is rotating in the direction opposed to that of the precession. The other field however will rotate in the opposite direction and represent the achievement of the resonant disturbance discussed above. The energy of the quantum associated with the high-frequency field will be

 $h\nu = \frac{h}{2\pi} \omega_{\rm L} = \frac{\mu}{I} H_{\rm C}.$

The energy of the magnetic substate corresponding to magnetic quantum number M_I is given by

 $\frac{M_I}{I} \mu H_C.$

Thus, as we would expect, the quantum of the resonant radio-frequency field has exactly the value required for a transition from a state with magnetic quantum number M_I to one with magnetic quantum number $M_I \pm 1$. We must take both

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