Determination of Some Nuclear Properties

8.1 Nuclear mass measurement: Introduction

Accurate determination of nuclear masses is of great importance in the development of the theory of nuclear structure. As discussed in Ch. II, the nuclear binding energy is related to the nuclear mass through the equation

\[ E_B(A, Z) = ZM_H + NM_n - M(A, Z) \]

where the masses are the atomic masses expressed in atomic mass unit in the unified scale (u). Its value is

\[ 1 \text{u} = 1.660566 \times 10^{-27} \text{kg} = 931.502 \text{MeV} \]

The binding energy per nucleon, known as the binding fraction \( f_B \), is a measure of the strength of binding of the nucleus:

\[ f_B = E_B/A \]

It is closely related to the mass defect \( \Delta M(A, Z) = M(A, Z) - A \) through the equation

\[ f_B = \frac{Zf_H + Nf_n - f_0}{A} \]

where \( f_H = 0.007825 \text{u} \) and \( f_n = 0.008655 \text{u} \) express the departure of the masses of the \(^1\text{H}\) isotope of hydrogen and neutron from unity.

Amongst different methods of atomic mass measurement accurately, historically the most important is the mass spectroscopic method developed by F.W. Aston. Mass spectroscopists express the atomic masses in terms of the mass defect \( \Delta M \) or to the closely related quantity packing fraction, \( f = M/A \).

8.2 Ion optics

Most mass spectroscopes employ a homogeneous magnetic field to deflect the positive ions from an ion source, which has an action on the ion beam, similar to that of a prism on a beam of light, i.e., the magnetic field produces a mass dispersion of the ion beam, which permits mass analysis of a composite beam consisting of ions of different masses. In addition, the magnetic field has a focusing action on the ion beam, similar to that of a lens on a light beam. This makes possible an initially diverging beam of ions of a given mass to be focused at a given point, thereby producing an ion beam of sufficient intensity for detection. For achieving greater accuracy in atomic mass determination, most high resolution mass spectroscopes employ a radial electric field in conjunction with a magnetic field, the two being arranged in tandem. Both the fields have some specific actions on the ion beam. For the full development of the scopes of these fields, it is necessary to gain proper understanding of the ion-optical properties of these fields.

(a) Direction focusing property of a homogeneous magnetic field:

The basic equation governing the deflection of an ion of mass \( M_0 \) and charge \( q \) in a magnetic induction field \( B \)

\[ Bqv_0 = M_0 v_0^2/r \]

where \( v_0 \) is the velocity of the ion and \( r \) is the radius of curvature of the path of the ions in the field, which acts perpendicular to the direction of the ion velocity.

Consider a beam of ions of mass \( M_0 \) and velocity \( v_0 \) to emerge from a point source \( O \) with a small angular divergence \( 2\alpha (\alpha < 1) \) and a spread in the radial velocity component \( v_{0r} \) which is proportional to the momentum of the ions. If the ions emerge from the source with a small angular divergence, the ions will be focused at a distance \( r = \frac{Bqv_0}{M_0} \) from the source, and the ion beam will be focused at a point. The electric field \( E \) is then used to achieve focusing in the axial direction as well.
about the mean ion direction. These enter a homogeneous magnetic field between the two sector-shaped pole-pieces of a magnet normal to the edge of the pole-pieces, as shown in Fig. 8.1. If the sector angle is \( \phi_m \) and the ion path is perpendicular to the magnetic field, then the ions follow a circular path of radius \( a_m \) and emerge from the field normal to the other edge of the pole-pieces, after being deflected through \( \phi_m \). The beam will then be focused at the image point I.

The above arrangement is like the optical combination of a prism and a cylindrical lens. The focal length of the lens is given by

\[
f_m = a_m / \sin \phi_m \quad \text{(8.2-1)}
\]

The object and the image distances \( l_o \) and \( l_i \) as shown in the figure are related through the equation

\[
(l_o - g_m) (l_i - g_m) = f_m^2 \quad \text{(8.2-2)}
\]

Here \( g_m \) is the distance of the principal focus from the boundary of the field. This is the distance from the exit boundary of the point to which a parallel beam of ions, incident normally on the entrance boundary, is focused. It is also the distance from the entrance boundary of the point source from which a slightly diverging beam of ions, incident on the boundary, emerge from the exit boundary as a parallel beam.

Eq. (8.2-2) shows that the object \( O \), the centre of curvature \( C \) of the sector and the image \( I \) lie on a straight line, as shown in the figure (see Ion Optics by L. Kerwin in Mass Spectrometry, Ed. C.A. McDowell, McGraw Hill).

If the object point is displaced through a distance \( b_m' \) normal to the mean ray, then the image is displaced through \( b_i' \). For an ion of mass \( M = M_0 (1 + \gamma) \) and velocity \( v = v_0 (1 + \beta) \) where \( \beta \) and \( \gamma \) are assumed to be small, it can be shown that \( b_m'' \) is given by the following relation:

\[
b_m'' = a_m (\beta + \gamma) \left( 1 + \frac{f_m}{l_m' - g_m} - b_m' \right) \quad \text{(8.2-4)}
\]

For the original ion group \( M_0, v_0 \) we get

\[
b'' = -b_m' \frac{f_m}{l_m' - g_m} \quad \text{(8.2-4a)}
\]

This gives the magnification

\[
G_m = \frac{b_m''}{b_m'} = - \frac{f_m}{l_m' - g_m} \quad \text{(8.2-5)}
\]

The negative signs in the Eqs. (8.2-4a) and (8.2-5) are due the inversion of the image.

For a symmetrical arrangement \( (l_m' = l_i') \) the magnification is unity.

For ions of a given mass \( M_0 \) (\( \gamma = 0 \)), emerging from a given object point with a velocity spread \( \pm v_0 \beta \) about the mean velocity \( v_0 \), there will be an image broadening given by

\[
\Delta M = \frac{M - M_0}{M_0} = \gamma = \frac{2S_0}{a_m \left( \frac{f_m}{l_m' - g_m} \right)(1 + \frac{f_m}{l_m' - g_m})} \quad \text{(8.2-9)}
\]

For a symmetrical arrangement, Eq. (8.2-2) gives \( l_m' - g_m = f_m \) so that the resolution becomes

\[
\frac{\Delta M}{M_0} = \frac{S_0}{a_m} \quad \text{(8.2-10)}
\]

For photographic method of detection of the ions, the image width as given by Eq. (8.2-4) is not further broadened. In electrical method of detection, an image slit of width \( S_i \) is placed in front of the detector, normal to the optic axis (mean ionic ray). In this case, the resolution becomes, for a symmetrical arrangement, \( (S_0 + S_i) < a_m \).

The ion focusing action of a magnetic field discussed above is known as first order focusing, in which all powers higher than the first of the angular divergence as also of the velocity spread \( \beta \), are neglected. The special case of semicircular focusing magnetic field was discussed in Ch. V.

The mass dispersion \( d \) for 1% change in the ion mass \( (\gamma = 1/100) \) in the case of a monoenergetic beam and a symmetrical arrangement can be obtained from Eq. (8.2-4) by putting \( b_m' = 0 \): It comes out to be
\[ d = K_m \gamma (\beta + \gamma) \]

\[ = a_m (\beta + \gamma) \left( 1 + \frac{f_m}{l_m - s_m} \right) \]

\[ = a_m \left( \beta + \frac{\gamma}{2} + \frac{\gamma}{2} \times 2 \right) = a_m \cdot \gamma / 2 \times 2 \]

\[ = a_m / 100 \] \hspace{8cm} (8.2-11)

\[ d \] has the dimension of length. It is measured in the plane normal to the optic axis.

(b) Direction focusing by the radial electrostatic field:

The field acting between the two plates of a cylindrical condenser is known as the radial electrostatic field. If the electric field at the mean radius \( a_e \) of the ion path midway between the two plates is \( E_0 \), then the field at the radius \( r = a_e (1 + p) \) (see Fig. 8.2) is given by

\[ E_r = a_e E_0 / r \] \hspace{8cm} (8.2-12)

Assuming the potential at the mean radius \( a_e \) to be zero, the potential at the radius \( r \) is given by

\[ V_r = E_0 a_e \ln (1 + p) = E_0 a_e p \] \hspace{8cm} (8.2-13)

Here \( p \) is assumed to be small.

Theoretical analysis shows that for a sector angle \( \phi_e \) of the electrostatic field, the object and image distances \( l_e' \) and \( l_e'' \) are related through the equation

\[ (l_e' - g_e) (l_e'' - g_e) = f_e^2 \] \hspace{8cm} (8.2-14)

where \( g_e \) gives the distances of the principal focus from the field boundaries given by

\[ g_e = \frac{a_e}{\sqrt{2}} \cot \sqrt{2} \phi_e \] \hspace{8cm} (8.2-15)

The focal length of the cylindrical electrostatic lens is

\[ f_e = \frac{a_e}{\sqrt{2} \sin \sqrt{2} \phi_e} \] \hspace{8cm} (8.2-16)

The focusing action of the radial electrostatic field discussed above gives first order focusing.

Eqs. (8.2-14) to (8.2-16) are analogous to the corresponding equations for the magnetic lens discussed earlier with the sector angle \( \phi_m \) being replaced by \( \sqrt{2} \phi_e \) and \( a_m \) by \( a_e / \sqrt{2} \).

(c) Double focusing principle:

Eqs. (8.2-4) and (8.2-17) give the positions of the images normal to the optic-axis for the magnetic and cylindrical electrostatic sector fields respectively. Each of them contains a term in \( \beta \), giving the velocity dispersion in the corresponding field. It is thus possible to arrange the two fields in such a way that the velocity dispersion produced by one will be counter-balanced by that produced by the other. If at the same time, conditions are fulfilled for the direction focusing by the combination, then the final image will be independent of both velocity and direction spreads of the ions emerging from the object slit. The combination will thus act as a double focusing arrangement.

Usually in a double focusing arrangement the image produced by a radial electrostatic field serves as the object for the following magnetic field. This means that we have to equate \( b_m' \) in Eq. (8.2-4) to \( b_e'' \) given by Eq. (8.2-17). This gives for the final image displacement in the magnetic field

\[ b_m'' = a_m (\beta + \gamma) \left( 1 + \frac{f_m}{l_m' - s_m} \right) - \frac{f_m}{l_m' - s_m} \times \left[ a_e (\beta + \frac{\gamma}{2}) \left( 1 + \frac{f_e}{l_e' - g_e} \right) - b_e' \frac{f_e}{l_e' - g_e} \right] \] \hspace{8cm} (8.2-20)

Using the above equations, it is possible to obtain the image displacement \( b_e'' \) for the ions emerging from an object point displaced through \( b_e' \) normal to the optic axis having mass \( M = M_0 (1 + \gamma) \) and velocity \( v = v_0 (1 + \beta) \):

\[ b_e'' = a_e (\beta + \frac{\gamma}{2}) \left( 1 + \frac{f_e}{l_e' - g_e} \right) - \frac{f_e}{l_e' - g_e} \] \hspace{8cm} (8.2-17)

For a monoenergetic ion beam \( 2\beta + \gamma = 0 \) for ions of all masses. Hence they are all focused at the same point and there is no mass dispersion. Ion groups of different energies, all emerging from the same object point, will be focused at different points. Thus cylindrical electrostatic field (electrostatic analyzer) acts as an energy-filter. In mass spectroscopy, it has little value by itself. Its importance lies in its combination with other fields to achieve double focusing.

Though the cylindrical electrostatic field does not produce mass dispersion, it produces velocity dispersion for a given mass \( (\gamma = 0) \) of the ions. The lateral displacement of the image for the velocity \( v = v_0 (1 + \beta) \) is given by (for \( b_e' = 0 \))

\[ y''(\beta) = K_e'' \beta \] \hspace{8cm} (8.2-18)

where the coefficient of velocity dispersion is

\[ K_e'' = a_e \left( 1 + \frac{f_e}{l_e' - g_e} \right) \] \hspace{8cm} (8.2-19)
There will be velocity focusing of the ion beam if the coefficient of $\beta$ in Eq. (8.2-20) vanishes. This happens when

$$a_m \left(1 + \frac{f_m}{l_m' - g_m}\right) = \frac{f_m}{l_m' - g_m} \times a_e \left(1 + \frac{f_e}{l_e' - g_e}\right) = 0$$

or,

$$a_m \left(1 + \frac{l_m' - g_m}{f_m}\right) = a_e \left(1 + \frac{l_e' - g_e}{f_e}\right) \quad \text{(8.2-21)}$$

From Eq. (8.2-21), the resolution and dispersion (for photographic detection) may be calculated. It is found that

$$\frac{\Delta M}{M} = \frac{2 S_0}{\alpha_e} \left(1 + \frac{l_e' - g_e}{f_e}\right) \quad \text{(8.2-22)}$$

and

$$d = \frac{a_m}{100} \left(1 + \frac{f_m}{l_m' - g_m}\right) \quad \text{(8.2-23)}$$

for 1% mass difference.

Eq. (8.2-22) shows that the resolving power ($M/\Delta M$) of a double focusing mass spectroscope depends only on the constants of the electrostatic analyzer and on the entrance slit width $S_0$. It increases linearly with the increasing value of $a_e$.

The dispersion of the instrument ($d$), on the other hand, depends on the constants of the magnetic analyzer.

### 8.3 Production and detection of positive ions

Different methods are used for the production of the positive ions, depending upon the element to be studied and upon the nature of study. We shall discuss a few of these in this section.

(a) **Gas discharge type of source**

Positive ion production in the discharge in a gas under low pressure was first observed by Goldstein in 1886. It was the main source of positive ions for a long time since then. In the earlier days of mass spectroscopy, these sources were extensively used by J. J. Thomson, F. W. Aston, K. T. Bainbridge and J. Mattauch.

The positive ions obtained from these sources are usually those of the gas used in the discharge tube or of the electrode material evaporated under the bombardment by cathode rays or by positive ions.

Ions of other substances, introduced as foreign materials into one or the other electrode may also be produced on evaporation.

After formation, the ions are usually accelerated towards a perforated cathode. The emergent ion-beam has a large energy-spread. The voltage used in the discharge tube usually ranges from $2 \times 10^4$ to $5 \times 10^4$ volts. Multiply charged ions are available from these sources. However, the sources are usually unsteady and do not give reproducible results.

With the development of the electron impact sources, the gas discharge sources have been largely superseded.

(b) **Surface ionization sources**

A.J. Dempster was the first to use this type of ion source in mass spectrometers in which positive ions are emitted from the surface of a metal filament coated with a salt of the substance to be investigated. Usually metals with high thermionic work-function are used as filament materials. Platinum has been used for this purpose, since it has the highest work-function. However, tungsten and tantalum are more widely used because they can withstand higher temperatures.

Surface ionization sources produce practically monoenergetic ions (energy spread 0.2 eV). So these sources are preferred for instruments possessing direction focusing property only. Another advantage of these sources is that only a small amount of the coating material is required for isotopic analysis.

In some cases, instead of a single filament, two filaments are used, one of which is coated with the salt and is at a relatively lower temperature. The salt evaporated from it impinges on the second filament, kept at a much higher temperature and is thereby ionized.

(c) **Electron impact sources**

In these sources, a beam of electrons, accelerated through a potential difference of several tens of electron volts, bombards a gas fed into an ionization chamber, which is thereby ionized. The ion-yield is maximum for an electron accelerating potential of 70-90 volts.

The ions obtained from these sources are nearly monoenergetic. The energy spread is usually as low as 0.05 eV. The ion yield can be considerably increased by using an axial magnetic field parallel to the electron path.

Ions of non-volatile substances can also be produced in these sources by incorporating an oven just above the ionization chamber.

The electron impact source is the most widely used in mass spectroscopy.

Besides the above, some of the other ion sources for mass spectroscopic work include the vacuum spark source (limited to double focusing instruments), arc sources which yield large ion current (useful for isotope separators) and field-emission ion source. In addition, an ion source based on the principle of Phillips ionization gauge has been developed which employs a cold discharge in a magnetic field (see also Ch. XII).

### Detection of positive ions

The positive ions can be detected either photographically or electrically. For photographic detection, special sensitive plates have been developed, mainly by Ilford Co. of England and Eastman Kodak Co. of U.S.A.
For electrical detection, the ions are collected in a Faraday cup and the very feeble positive ion current measured by a sensitive low current measuring device. In the early days, electrometers were employed which were later superseded by the electrometer valves. The electrometer valve constitutes the input stage of a dc amplifier. To overcome the inherent instabilities of these dc amplifiers, special balanced circuits have been developed (see § 7.23). Varying degrees of negative feedback have also been employed for the same purpose.

Vibrating reed electrometers are now-a-days used extensively for the detection and measurement of the positive ion current. These have been described in § 7.23.

Electron multipliers are also used as detectors of positive ions. There are usually 10 to 14 stages of dynodes which result in enormous gains. The method is extremely sensitive and has very fast response. Individual positive ions can be detected by this method. Scintillation detectors have also been used for the detection of positive ions, which are accelerated to high voltages before falling on the scintillator.

8.4 Dempster's semi-circular focusing mass spectrometer


Dempster built a semi-circular type mass spectrometer at the University of Chicago in 1918. A schematic diagram of his instrument is shown in Fig. 8.3.

The ions from an ion source enter the transverse magnetic field through the source slit S₁ after being accelerated through the voltage V. The source slit is located just at the edge of the magnetic field. Dempster's mass spectrometer possesses direction focusing property. The slightly diverging beam of ions, after deflection through 180° by the magnetic field, is focused at a point S₂ at a distance from S₁ along the edge of the magnetic field and is collected by a collector plate A as shown. The magnetic field B acts perpendicular to the plane of the paper. The collector current is measured by a quadrant electrometer.

The kinetic energy of the ions of charge q and mass M is given by \[ \frac{1}{2} Mv^2 = qV. \] If the radius of curvature of the ion-path in the field be \( R \), we can write

\[ \frac{Mv^2}{R} = Bqv \]

which gives

\[ Mv = BqR \]

and

\[ qV = \left( \frac{Mv^2}{2M} \right) = B^2q^2R^2/2M \]

So we get

\[ \frac{q}{M} = \frac{2V}{B^2R^2} \] \hspace{1cm} (8.4-1)

The ion groups of different masses are focused into the collector for detection by varying the accelerating potential \( V \), holding the magnetic field (B) constant. The distance between \( S_1 \) and \( S_2 \) is equal to the diameter \( 2R \) of the ion path.

Since there is no velocity focusing, the ion beam must have as little velocity spread as possible. The ions are usually produced with low kinetic energy by heating a salt on a metallic filament or by bombarding a salt with electrons.

Eq. (8.4-1) shows that the ions are deflected according to their \( M/q \) values.

With his instrument, Dempster discovered and made accurate abundance determination of the isotopes of magnesium, lithium, potassium, calcium and zinc.

Dempster type instruments possessing direction focusing property are not very suitable for accurate mass determination. They are primarily useful for isotopic abundance determination and ionic yield measurement for different types of ion sources.

The ion current measured by the electrometers gives a measure of relative abundance of the isotope. A typical result is shown in Fig. 8.4.

\[ \frac{Mv^2}{R} = Bqv \]

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and

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isotopes of neon, $^{20}\text{Ne}$ and $^{22}\text{Ne}$, first suspected by Thomson. As more elements were studied, such as chlorine, mercury, nitrogen and the inert gases, Aston proved conclusively that the masses of all atoms were close to integers, when expressed in term of the atomic mass of oxygen. This was the famous whole number rule propounded by Aston.

The principle of Aston's mass spectrograph, which possesses velocity focusing property, can be understood by referring to fig. 8.5a.

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**Fig. 8.5. (a) Principle of Aston's mass spectrograph. (b) Locus of the ion focusing points in Aston's mass spectrograph.**

The positive ions produced in a discharge tube possess a wide range of energies. They are collimated by two extremely narrow slits $S_1$ and $S_2$. The ion beam, collimated in the form of a very thin ribbon having very little angular divergence, enters the electric field $X$ between two parallel metal plates $P_1$ and $P_2$ and is deflected through an angle $\theta$, which depends on the velocity $v$ of the ion. If the ions entering the electric field have a velocity spread between $v$ and $(v + dv)$, then they will be deflected through a range of angles between $\theta$ and $(\theta + d\theta)$ determined by the width of the exit slit $D$ from the electric field.

As was proved in Ch. II, Vol I, the deflection of an ion of mass $M$ and charge $q$ in the electric field is inversely proportional to the square of the ion velocity and can be written as

$$\theta = K_e \frac{Xq}{Mv^2} \quad \ldots (8.5-1)$$

where $K_e$ is a geometrical factor which is a constant. We thus have for ions of a given specific charge $q/M$

$$\theta v^2 = \text{constant} \quad \ldots (8.5-2)$$

Differentiating we get

$$\theta v^2 dv + 2\theta \nu dv = 0$$

which gives

$$\frac{d\theta}{\theta} + 2\nu dv/v = 0 \quad \ldots (8.5-3)$$

Eq. (8.5-3) gives the range of velocities $d\nu$ through which the ions within the velocity range $dv$ are deflected.

After emerging from the electric field, the ion beam enters a homogeneous magnetic field ($B$) at a mean distance $b$ from the former. The magnetic field, which is perpendicular to the plane of the paper, is produced by an electromagnet. Under its action the ion beam is deflected in the same plane as the electric deflection and in the opposite sense to the latter. As proved in Vol. I, the magnetic deflection is given by

$$\phi = K_m \frac{Bq}{Mv} \quad \ldots (8.5-4)$$

$K_m$ is a constant, depending on the geometry of the arrangement. Eq. (8.5-4) gives

$$\phi v = \text{constant} \quad \ldots (8.5-5)$$

Differentiating we get

$$\nu d\phi + \phi \nu dv = 0$$

or,

$$\frac{d\phi}{\phi} + \nu dv/v = 0 \quad \ldots (8.5-6)$$

$d\phi$ is the angular range through which the ions with a velocity spread $dv$ are deflected by the magnetic field. By properly adjusting the magnetic field, it is possible to compensate the electric dispersion $d\theta$ completely and thereby refocus the ion beam at some distance $r$ from the magnetic field. The condition for this is that the linear electric dispersion $(b + r)d\theta$ must be equal and opposite to the linear magnetic dispersion $r d\phi$ at the focusing point:

$$(b + r)d\theta = r d\phi \quad \ldots (8.5-7)$$

Eqs. (8.5-3) and (8.5-6) give

$$d\theta/\theta = 2d\phi/\phi \quad \ldots (8.5-8)$$

We then get from Eqs. (8.5-7) and (8.5-8)

$$\frac{d\theta}{\theta} = \frac{r}{b + r} = \frac{2\theta}{\phi}$$

or,

$$\frac{r}{b - \phi} = \frac{2\theta}{\phi - 2\theta} \quad \ldots (8.5-9)$$

Eq. (8.5-9) gives the ion-focusing distance $r$ from the magnetic field for ions of different $q/M$.  

---
If a photographic plate is placed along the locus of the ion focusing points, then the ions of different \( q/M \) will be focused at different points on this plate.

To determine the locus of the ion-focusing points, we refer to Fig. 8.5b. In the figure, M and O are the centres of the electric and magnetic field regions and F is the ion-focus point. If we draw two straight lines OX and OF making the angles \( 20 \) and \( \varphi \) respectively with the extended portion of the straight line MO, then the angle between OF and OX is \( (\varphi - 20) \). If MN represents the direction of the ion beam entering the electric field, the angle between MN extended and MO is \( \theta \). We draw a line OY perpendicular to OX; then \( x_F = FQ \) and \( y_F = FP \) are the distances of F from the two axes OX and OY respectively.

Eq. (8.5-9) shows that when \( \varphi = 20 \), the ions will emerge from the magnetic field as a parallel beam, since \( r = \infty \) in this case. To focus the ions at a finite distance from O, we must have \( \varphi > 20 \). The values of \( x_F \) and \( y_F \) for small \( \theta \) and \( \varphi \) can be seen to be:

\[
x_F = QF = r \cos (\varphi - 20) \\
y_F = OQ = r \sin (\varphi - 20) = r (\varphi - 20)
\]

We then have, using Eq. (8.5-9):

\[
y_F = OQ = r (\varphi - 20) = b - 20
\]

In Aston’s apparatus, \( b \) and \( \theta \) are constants, so that \( y_F \) is constant which means that the distances of the different ion-focusing points from the axis OX are the same. So the locus of the ion-focus points is the straight line drawn parallel to OX. From Fig. 8.5b, it can be seen that the angle between MO and MF is \( 20 \). So MF and FQ must lie along the same straight line and the photographic plate must lie along this line which makes the angle \( \varphi \) with the direction MN along which the ions enter the electric field.

In a constant electric field, the ions of different \( q/M \) but having the same energies \( MV^2/2 \) suffer the same electric deflection \( \theta \) (see Eq. 8.5-1). After emerging from the magnetic field, they are focused at different points on the photographic plate.

In Aston’s mass spectrograph, the incident ions of the same \( q/M \) having negligible angular spread but with a small velocity spread \( (dv) \) are all focused at a single point on the photographic plate. Hence it is known as a velocity focusing mass spectrograph.

**Accurate determination of atomic masses with Aston’s mass spectrograph**

The resolution of the first mass spectrograph built by Aston was 1 part in 130. He could measure atomic masses with an accuracy of about 1 part in \( 10^3 \). Later, with improved versions, the accuracy of mass measurement achieved by him was about 1 part in \( 10^5 \). One of his later instruments is shown in Fig. 8.6.

B is a large glass bulb, within which the positive ions are produced by gas discharge. Ions of the same charge \( q \) but different masses \( M \) acquire the same energy \( qV \) by being accelerated through the same accelerating voltage \( V \) and are highly collimated by passing them through the system of narrow slits \( S_1, S_2 \) etc. The collimated beam then enters the electric field between the two slightly curved plates \( J_1 \) and \( J_2 \) and is deflected thereby. The deflected beam, after passing through the exit slit \( D \), falls on the photographic plate \( A \), after suffering the magnetic deflection.

![Fig. 8.6. A later model of Aston’s mass spectrograph.](image)

Since the slits \( S_1, S_2 \) etc. have small but finite lengths perpendicular to the plane of the paper, the refocused ions produce a number of mass-lines on the plate, instead of points.

The whole apparatus was kept under high vacuum. There was arrangement for making a fiducial mark on the photographic plate with the help of a light source.

Aston first calibrated the photographic plate by measuring the distances from the fiducial point of the mass-lines produced by ions of known masses. A plot of these distances against the known isotopic masses gave a calibration curve, with the help of which an unknown isotopic mass could be determined by measuring the distance of the mass-line produced by the corresponding ions from the fiducial point. Aston used the oxygen-16 scale for the atomic masses. As stated in Ch. II, this has since been replaced by the carbon-12 scale.

Later Aston used the bracketing method for more accurate determination of the atomic masses.

Consider ions of masses \( M_1 \) and \( M_2 \) carrying equal charges to be deflected through the same angle in the electric field. If the corresponding fields are \( X_1 \) and \( X_2 \), then from Eq. (8.5-1) we get:

\[
\frac{X_1}{M_1 v_1^2} = \frac{X_2}{M_2 v_2^2}
\]

where \( v_1 \) and \( v_2 \) are the velocities of the two types of ions. If the potential difference between the plates \( J_1 \) and \( J_2 \) be \( V_1 \) and \( V_2 \) in the two cases, we get:

\[
\frac{M_1 v_1^2}{M_2 v_2^2} = \frac{V_1}{V_2}
\]

... (8.5-10)
The two groups of ions, suffering equal electric deflections, enter the magnetic field. If the magnetic induction field $B$ is kept the same in the two cases, then the corresponding magnetic deflections are

$$\phi_1 = K_m Bq_1/M_1 v_1, \quad \phi_2 = K_m Bq_2/M_2 v_2$$

so that

$$\phi_1/\phi_2 = M_2 v_2/M_1 v_1$$

If the magnetic deflections are also equal in the two cases ($\phi_1 = \phi_2$), then the two groups of ions are focused at the same point on the photographic plate. We then get

$$M_1 v_1 = M_2 v_2 \quad \text{...(8.5-11)}$$

The conditions (8.5-10) and (8.5-11) can both be satisfied if

$$V_1 = V_2 \quad \text{and} \quad M_2 = n M_1 \quad \text{(say)}$$

Thus in order to focus ions of mass $M_2 = n M_1$ at the same point as the ions of mass $M_1$ on the photographic plate, the potential differences causing the electric deflections for the two groups of ions should be related through the equation $V_2 = V_1/n$. In this case, the two mass-lines coincide.

If the p.d. $V_2$ is not exactly equal to $V_1/n$ then the two mass lines will not coincide. We now consider two cases such that $V_2$ is made slightly greater than $V_1/n$ in one case ($V_2 = V_1/n + \Delta V$) while in the other case, it is less than $V_1/n$ by the same amount ($V_2 = V_1/n - \Delta V$). Then two mass-lines will be produced on the photographic plate, symmetrically spaced on either side of the mass-line due to $M_1$. In practice, the ratio $V_1/V_2 = n$ is gradually altered till this condition is achieved. From the corresponding value of $n$ the mass $M_2 = n M_1$ is determined.

Usually the value of $n$ is approximately known. As an example, for the two ions $^{16}O^+$ and $^{32}S^+$, $n$ is approximately $\frac{1}{2}$. If $n$ were exactly $\frac{1}{2}$, then the mass-lines for $^{32}S^+$ would be symmetrically spaced on either side of the $^{16}O^+$ line. However, since $M(\cdot^{16}O^+) = M/2(\cdot^{32}S^+)$, the two lines due to the latter are spaced asymmetrically on either side of the mass-line due to the former.

In some cases, by measuring the above mentioned asymmetry it is possible to determine the mass difference between the two ions quite accurately with the help of a calibration curve.

### 8.6 Bainbridge's first mass spectrograph

K.T. Bainbridge in the U.S.A. built a mass spectrograph in 1932 incorporating a Wien velocity filter. The instrument is shown in Fig. 8.7. It is a $180^\circ$ magnetic focusing instrument like Dempster's mass spectrometer. The ions are detected photographically. Ions of different values of $q/M$ produce different mass-lines on the plate.

Before the ions enter the magnetic analyzer, they pass through the velocity filter, which consists of two parallel metal plates $P_1, P_2$ with a small gap between them. A collimated beam of ions enters the gap between the two plates parallel to the latter. An electric field $X$ acts between these plates which is in the plane of the paper perpendicular to the incident ion direction. A magnetic induction field $B_1$ also acts in the same region, perpendicular to the plane of the paper, so that the electric and magnetic forces on the ions are in the same plane. The strengths of the two fields are so adjusted that the forces acting on the ions due to them are equal and opposite. As a result, these ions are able to pass through the filter without deflection. The condition for this is

$$B_1 q v = X q$$

or,

$$v = X/B_1 \quad \text{...(8.6-1)}$$

The above equation shows that ions of different $q/M$, having the same velocity, can pass through the filter.

Because of the very small gap between $P_1$ and $P_2$ the velocity selection could be done very accurately by the velocity filter so that there was very little velocity spread of the emergent ion beam.

These ions enter the magnetic analyzer through the slit $S$, and after suffering a deflection of $180^\circ$ fall on the photographic plate $P$. Ions of different $q/M$ entering the magnetic analyzer field $B$, with the same velocity $v$, are brought to focus at different points on the photographic plate. If $R$ is the radius of curvature of the path of the ions of a given $q/M$ we can write

$$B q v = M v^2 / R$$

$$M/q = B R / v$$

Thus $R$ is linearly proportional to the ion mass $M$ for the same ionic charge $q$. This means that the distance between the mass-lines on the photographic plate ($2\Delta R$) is linearly proportional to the mass difference $\Delta M$. This is a definite advantage over Aston's mass spectrograph.

The Wien velocity filter used by Bainbridge possesses direction focusing property.

The addition of the velocity filter to Bainbridge mass spectrograph greatly improved its resolution which was ~ 1 in 500 in his later instruments.

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55 See ibid
Bambridge used his instrument to measure the masses of many lighter atoms. These included the deuterium atom and the atoms involved in the nuclear reaction $^7\text{Li} + ^1\text{H} \rightarrow ^2\text{He}$. This work provided the first experimental test of Einstein's mass energy relationship.

### 8.7 Double focussing mass spectroscopes

Double focussing mass spectroscopes were developed independently by Dempster, Bainbridge, J. Mattauch and R. Herzog, A.O. Nier and others for the purpose of precise atomic mass determination. We shall briefly describe a few of these below.

(a) **Dempster's double focusing mass spectrograph**

This instrument, shown schematically in Fig. 8.8, was completed in 1935. It consists of a $90^\circ$ radial electrostatic analyzer, followed by a semicircular magnetic analyzer. The image formed by the electrostatic analyzer is located at the effective boundary of the magnetic field so that $t'_{m} = 0$. The final image is formed at the exit boundary of the magnetic field ($t'_{m} = 0$). Velocity focusing occurs for one radius of curvature in the magnetic field determined by Eq. (8.2-21) which gives $a_{m} = 1.15 a_{e}$ for the parameters shown in the figure. Photographic method of detection was used.

Dempster's original apparatus achieved a resolution of 1 in 3000 for $S = 8.5 \text{ cm}$ and principal slit width of 0.0025 cm. Many larger models of the apparatus were built later.

One such instrument built by H.E. Duckworth (1960) at the University of McMaster in Canada was much bigger in size. With $a_{e} = a_{m} = 2.74 \text{ m}$ and $t'_{e} = t'_{e} = 0.35 a_{e}$, the resolution achieved was in excess of 1 in 100,000.

(b) **Bainbridge and Jordan's mass spectrograph**

This instrument built in 1936, used a $\pi/\sqrt{2}$ electrostatic analyzer followed by a $60^\circ$ sector field magnetic analyzer (see Fig. 8.9). Both fields are employed symmetrically with $t'_{e} = t'_{e} = 0$ and $t'_{m} = t'_{m} = \sqrt{3} a_{m}$. The resolution achieved was 1 in 10,000 for a principal slit width of 0.0025 cm.

A larger instrument of the same type with many technical improvements was built by K. Ogata and H. Matsuda (1953) which attained resolution in the range 1 in 40,000 to 1 in 60,000.

(c) **Mattauch-Herzog mass spectrograph**

This is a very remarkable instrument, since it possesses double focussing at all masses. It was built in Germany around 1934. As shown schematically in Fig. 8.10, it consists of a $\pi/4\sqrt{2}$ electrostatic analyzer followed by a $90^\circ$ magnetic analyzer. Both the analyzers use asymmetrical arrangement. The entrance slit is located at the principal focus of the e.s. analyzer so that a parallel beam emerges from the latter (see § 8.2) and enters the magnetic analyzer. Consequently the final image is located at the principal focus of the latter.

The velocity focusing condition (Eq. 8.2-21), can be shown to transform to

$$\sin \phi_{m} = -\sqrt{2} \sin \sqrt{2} \phi_{e}$$

(8.7-1)

This is independent of $a_{m}$ as required. $\phi_{m}$ and $\phi_{e}$ are in opposite directions.

The photographic plate is located at the exit boundary of the magnetic analyzer, so that $\phi_{m} = 90^\circ$ and hence $\phi_{e} = \pi/4 \sqrt{2}$. As a result $t'_{e} = a_{e} / \sqrt{2}$. The resolution, dispersion and magnification are $2S/a_{e}$, 0.007$a_{m}$ at 1% mass difference and $a_{m}/a_{e}$, respectively.

In their first instrument, Mattauch and Herzog attained a resolution of 1 in 5600 for $S = 0.0025 \text{ cm}$ and $a_{e} = 28 \text{ cm}$. Later models of the instrument have attained resolutions in excess of 1 in 100,000.
Second order double focusing: The double focusing mass spectrometers discussed above use first order focusing in which the second and higher order terms in the angular spread \( \alpha \) and velocity spread \( \beta \) are neglected. As a result, there are image- aberrations which affect achievement of very high resolution.

H. Hintenberger, H. Wende and L. A. König have investigated the possibility of achieving second order direction focusing in the Mattauch-Herzog instrument with first order velocity focusing at all masses. They have shown that it is possible to attain second order direction focusing at one mass near the centre of the photographic plate by suitably choosing the ratio \( a_i/\alpha_w \). A large mass spectrograph of the Mattauch-Herzog type was built by Mattauch, Hintenberger and others which has second order direction focusing at one mass in addition to usual first order double focusing at all masses.

The theoretical resolving power with a slit width of 1 micron is \( 2.7 \times 10^6 \). A dispersion of 13.9 mm for 1% mass difference was obtained.

Usually \( \alpha \) is much larger than \( \beta \) so that the most important second order aberration arises due to neglecting \( \alpha^2 \). E.G. Johnson and A.O. Nier have developed a theory of the two field combination in which the second order angular aberration is eliminated. Based on this theory, Nier and Roberts (1951) and Johnson and Nier constructed double focusing mass spectrometers with direction focusing of the second order and velocity focusing of the first order at a given point. As stated above, the Mattauch-Herzog instrument possesses second order direction focusing property at the position given by \( a_i/\alpha_w = 1.683 \). The 2.54 m radius instrument at the Argonne National Laboratory in the U.S.A. (1967) possesses second order direction focusing.

H. Hintenberger and L.A. König investigated theoretically the second order focussing properties of cyndrical electrostatic analyzer and uniform magnetic fields and have listed the parameters of such arrangements in extensive tabular forms (1959). In addition, toroidal electrostatic analyzers and non-uniform magnetic fields have focussing properties in both radial and axial directions. H. Ewald and H. Liebl have investigated the second order focusing properties of these arrangements.

T. Matsuo, H. Matsuda, Y. Fujita and H. Wollnik (1965) have developed a computer program for third order ion optics ("TRIO").

Based on some of these theoretical investigations, a number of very high resolution instruments have been constructed in different parts of the world. At the University of Manitoba in Canada, R. C. Barber H. E. Duckworth and others (1971) have constructed an instrument (MANITOBA II) on the basis of Hintenberger and König's calculations. The instrument has been used for precise atomic mass determination with a resolving power (FWHM) of \( 3 \times 10^6 \). A novel type mass spectrometer having a toroidal electrostatic field followed by a non-uniform magnetic field varying as \( 1/r \) and then by a uniform magnetic field was constructed by H. Matsuda, S. Fukumoto and others at the Osaka University in Japan. (OSAKA II) in 1966. Both photographic and electrical methods of detection were used with resolving powers of \( 1.2 \times 10^6 \) (mass dispersion 4.75 cm) and \( 2 \times 10^5 \) to \( 10^6 \) respectively. The instrument has been used for precise mass determination.

8.8 Doublet method of accurate comparison of atomic masses

Comparison of atomic masses is usually done by the doublet method. By a doublet is meant a pair of close lying mass spectral lines due to two types of ions having nearly equal values of the specific charge \( (q/m) \). The two types of ions must of course have exactly the same value of \( A/n \) where \( A \) is the mass number or sum of the mass numbers of any type and \( n \) is the charge of the ion in electronic charge unit. Thus a doubly charged ion can form a doublet with a singly charged ion of nearly half the atomic mass of the former. An example is the doublet formed by the pair \(^{32}\text{S}^{2+}\) and \(^{16}\text{O}^+\) ions \((A/n=16)\). If the mass of one of the members of the doublet is known, that of the other may be calculated from the knowledge of the doublet separation and the dispersion of the mass spectograph.

The doublet method can in principle be applied even when the mass spectral lines are widely separated. In practice, because of non-uniform dispersion, only close lying doublets can be compared accurately.

Comparison is usually made with carbon or some compound of carbon with hydrogen. Since \(^{13}\text{C}\) is taken to have the atomic mass exactly equal to 12, such comparison can yield very accurate values of the atomic masses of the other species of ions in the pair.

The accuracy of atomic mass determination is usually very great, even when the accuracy of measurement of the doublet separation is much less. For example, if the accuracy of measuring the mass dispersion is \( 1 \) part in \( 10^3 \), then the fractional mass difference of the doublet \(^{2}H^+\) amounting to \( 1 \) part in \( 1300 \) means a difference of \( 1 \) part in \( 1 \times 10^6 \) in the mass ratio of the two types of ions or in the mass determination of \(^{2}\text{H}\), assuming that the mass of \(^{1}\text{H}\) is known very accurately.

A number of important fundamental mass doublets is of great practical value for the purpose of mass comparison. For example we consider the following three doublets, for which the measured doublet separations are

\[
\begin{align*}
\left( ^{12}\text{C}\right)^{+} - ^{16}\text{O}^+ & = \alpha, \quad (A/n = 16) \\
\left( ^{12}\text{C}\right)^{+} - \left( ^{32}\text{S}^{16}\text{O}^+\right)^+ & = \beta, \quad (A/n = 48) \\
\left( ^{16}\text{O}^+\right)^{+} - ^{32}\text{S}^{+} & = \gamma, \quad (A/n = 32)
\end{align*}
\]

From these equations it is possible to obtain the masses of \(^{1}\text{H},^{16}\text{O}\) and \(^{32}\text{S}\) atoms assuming \(^{12}\text{C}\) atomic mass to be 12.

From the above we can write

\[
\begin{align*}
3M(12\text{C}) + 12M(1\text{H}) - 3M(16\text{O}) & = 3\alpha \\
4M(13\text{C}) - M(32\text{S}) - M(16\text{O}) & = \beta
\end{align*}
\]

\[S_{\text{mass}}\]
\[ 2M(^{16}\text{O}) - M(^{32}\text{S}) = \gamma \]

We then get
\[ 3\alpha - \beta + \gamma = 12M(^{1}\text{H}) - M(^{12}\text{C}) \]

or,
\[ M(^{1}\text{H}) = \frac{1}{12} [M(^{12}\text{C}) + 3\alpha - \beta + \gamma] \]

\[ = 1 + \frac{1}{12} (3\alpha - \beta + \gamma) \]

Similarly we get
\[ M(^{16}\text{O}) = 16 + \frac{\gamma - \beta}{3} \]

\[ M(^{32}\text{S}) = 32 - \frac{2\beta + \gamma}{3} \]

Since \( \alpha, \beta \) and \( \gamma \) are known from measurements, it is possible to determine the masses.

Another group of fundamental doublets of importance are:

- \(^{1}\text{H}^2 - ^{2}\text{H}^2\) \((A/n = 2)\)
- \(^{2}\text{H}^4 - ^{12}\text{C}^4\) \((A/n = 6)\)
- \(^{12}\text{C}^4\text{H}^2 + ^{16}\text{O}^4\) \((A/n = 16)\)

The measured mass differences in these cases yield the masses of \(^{1}\text{H}, ^{2}\text{H}\) and \(^{16}\text{O}\) atoms.

A variation of the doublet method, known as the peak matching technique, is applicable in the case of electrical method of detection.

In the photographic method of detection, the precision with which the position of a mass spectral line can be determined is about \(1/50\) of the line-width. So, with a resolution of \(1\) in \(20,000\) of the mass spectograph, the mass determination can be made with an accuracy of \(1\) part in \(10^6\).

With the peak matching technique, it is possible to locate the ion current peak with an accuracy of \(1\) part in \(10^3\) or better. So it is possible to achieve an accuracy of \(2\) parts in \(10^8\) in mass measurement. The basic idea underlying the method will be discussed in § 8.9.

8.9 Special types of high resolution mass spectrometers

(I) Mass spectrometers using cyclotron principle

The operation of these instruments is based on the fact that the ions describe circular paths in a homogeneous magnetic field \(B\) with a time period \(T\) which is independent of their velocity. Thus, for ions of mass \(M\) and charge \(q\), the magnetic force is

\[ Bqv = \frac{Mv^2}{r} \]

where \(v\) is the ion velocity and \(r\) is the radius of its trajectory. So we get

\[ v = \frac{M}{Bq} \]

and

\[ T = \frac{2\pi r}{v} = \frac{2\pi M}{Bq} \]  

Thus \(T\) depends on the specific charge \(q/M\) of the ions. This fact permits mass analysis through the measurement of the time of flight of the ions from the source to the detector or of the cyclotron frequency \(f = 1/T = Bq/2\pi M\).

As can be seen from Fig. 8.11, ions starting from a given point in a homogeneous magnetic field \(B\) are all focused at the starting point, if they have all the same initial velocity \(v\) without any component parallel to \(B\), irrespective of the velocity \(v\) and the direction of emission from the source. This means that there is perfect double focusing of the ions.

![Fig. 8.11 Trajectories of monoenergetic ions of a given mass emitted from a point source in a homogeneous magnetic field.](image)

If there is no other deflecting field acting on the ions, they will all hit the back of the ion source after describing one complete cycle. Hence the arrangement will be of little practical value.

However, if the ions have a velocity component parallel to \(B\), their orbits will be drawn out into helix with the axis parallel to \(B\). After describing an integral number of complete cycles, the ions of the same specific charge \((q/M)\), having different initial velocities and coming out in different directions from the source, will be perfectly double focused as before. The time period will also remain the same. Alternatively, if the ion velocity is changed during revolution in a plane, they will describe spiralling path.

Both the above principles have been utilized in the construction of high resolution mass spectrometers. We shall describe very briefly two types of instruments based on these principles and a third type (mass synchronometer) in more detail.

(a) Helical path mass spectrometer:

Following an original suggestion of S.A. Goudsmit, the first mass spectrometer based on the above principle, in which the ions enter the homogeneous magnetic field, was constructed by P.I. Richards and Goudsmit. All ions emerging from a point source are focused along a sharp focal line, after describing an integral number of complete cycles independently of their specific charge. However, the times of arrival of the ions of different \(q/M\) are different.

The instrument of Hays et al used a pulsed ion source. The time of arrival of the ions after seven complete cycles was measured.

The masses of the ions could be measured with an accuracy of about \(0.001\) u.
Another instrument, known as the omegatron, was constructed by J.A. Hippie, H. Sommer and M.A. Thomas in which the ions described spiralling paths. The instrument may be regarded as a miniature cyclotron.

Unlike in a cyclotron (see Ch. XII) no ‘dee’ is used in this instrument, the rf voltage being applied between two parallel plate electrodes and also to the guard rings to ensure a uniform field. The rf field acts at right angles to the steady and homogeneous magnetic field. Under resonance condition between the time period of the ion path (which is independent of v) and the time period of the applied rf field, the orbit, radius is given by $r_0 = \frac{E_0 t_0}{2B}$ where $E_0$ is the amplitude of the rf field. This shows the spiralling nature of the ion orbit (see Fig. 8.12).

The resolving power of the instrument is given by

$$\frac{M}{\Delta M} = \frac{\pi r_0}{2T_0}$$

...(8.9-2)

where $T_0$ is the time period of the ion orbit at resonance and $t_0$ is the time required by the ions to reach the collector at resonance. The resolving power is thus proportional to the number of revolutions $n = t_0/T_0$ made by the ions before reaching the collector.

The first omegatron built by Hippie et al consisted of two 3 cm x 5 cm parallel (rf) plates, 2 cm apart, with eight equally spaced parallel guard rings. The resonance peaks could be scanned by varying the rf field. For high resolution, the magnetic field was varied. The number of revolutions $n$ varied from 3000 to 7000. The resolving power was $10^4$ for low masses.

The instrument has been used mainly for the determination of the proton magnetic moment $\mu_p$ by measuring the cyclotron frequency and the nuclear resonance frequency for the protons in the same magnetic field.

(c) Mass synchronometer:

This instrument, developed by L.G. Smith (1951) is shown schematically in Fig. 8.13. The positive ions from the ion source after emerging through the slit $S_1$ describe a circular trajectory in a perpendicular magnetic field with a radius $r$ determined by Eq. (8.9-1). After describing a half cycle, they pass through the slits within the ‘pulser’ and are subjected to a local modulating potential.

In the first model, the modulating potential consisted of negative rectangular pulses of 1 μs duration occurring at regular intervals which could be varied. The first pulse reduced the ion velocity, so that after emerging through $S_3$ the ions followed the trajectory 2 of smaller radius. After a number of revolutions in this trajectory the ion velocity was reduced further by a second pulse, so that the ions followed the trajectory 3 of still smaller radius and entered the collector after half a cycle through the slit $S_2$.

It was found that ions of mass number 28 accelerated through 250 μs reached the collector after describing 90 revolutions covering a total path of 72 m. The resolution at half maximum was 1 in 24,000. However, the intensity was very low.

In a second model built by Smith in 1952, $S_3$ was connected to an oscillator which caused harmonic modulation of the orbit radius. It was arranged that the ions described one complete revolution in $\frac{1}{2}$ cycles of the rf voltage, so that the ions reached the pulser in such a phase that there was demodulation of the ion beam. Thus most of the ions in the original beam reached the detector which increased the intensity of the detected beam considerably. In the actual operation, demodulation was not complete after one revolution so that the resolution was much below expectation.

In a later improved model built by Smith and C.C. Damm in 1956, resolution of 1 in 10,000 to 1 in 25,000 for all masses below 250 was achieved.
The mass difference between two ion masses $M_1$ and $M_2 = M_1 + \Delta M$ is given by either $M_1/\Delta M = f_2/\Delta f$ or $M_2/\Delta M = f_1/\Delta f$ where $f_1$ and $f_2$ are the cyclotron frequencies for the two ions and $\Delta f = |f_1 - f_2|$.

**Peak matching technique:**

Smith and Damm used peak matching technique for measuring the frequency difference $\Delta f$ with high precision. The principle of the method can be understood by referring to Fig. 8.14. The frequency of the rf voltage is modulated with a sawtooth voltage in phase with the horizontal sweep of an oscilloscope, while the amplified output from the ion-collector is applied to the vertical deflecting plates of the oscilloscope. This allows the mass spectral lines to be displayed on the oscilloscope screen. At the same time, the rf frequency is changed from $f_1$ (for mass $M_1$) to $f_2$ (for mass $M_2$) at the end of each sweep. Thus the two peaks appear on the screen one after the other, which are seen by the eye simultaneously due to persistence of vision. Their positions can then be matched with a high degree of accuracy and the frequency change required to produce the matching can be determined very accurately.

In a variation of the arrangement, a square wave voltage of high frequency is fed to the vertical plates of the oscilloscope, which splits one of the peaks to appear as two, one above and one below the other peak. Matching of the peaks can then be made with very high accuracy.

As stated earlier, the peak matching technique has made possible very accurate mass comparison. Nier has used this technique in a modified form in his double focusing mass spectrometer.

**Peak matching technique for deflection type instruments:**

The peak matching technique is essentially a doublet method applicable in the case of electrical detection of the ions in a mass spectrometer and hence is applicable in the case of deflection type instruments, as will be discussed below.

Consider two groups of ions of masses $M_1$ and $M_2$ initially at rest at the same point. They will follow the same trajectory within the mass spectrometer for any (constant) magnetic field if the electric fields $E_1$ and $E_2$ for the two groups are so adjusted that

$$M_1E_1 = M_2E_2$$

or,

$$M_1V_1 = M_2V_2$$

where $V_1$ and $V_2$ are the potentials on the relevant electrode.

In a typical arrangement, a master trigger, supplying regular pulses starts an oscilloscope sweep circuit. The sawtooth voltage from the oscilloscope controls the output current from a power amplifier, which produces a small sawtooth that is used to modulate the ion beam across the collector slit. The ion current is detected by an electron multiplier whose output is amplified and displayed by the oscilloscope, from which the sawtooth originated. Thus the peak for a given ion mass $M_1$ is displayed on the oscilloscope screen.

If now the potential on the relevant electrode is changed according to Eq. (8.9-4) given above, then the peak for the ion mass $M_2$ appears exactly superimposed on that of $M_1$. The height of the peaks may be matched by adjusting the accelerating potentials ($V_a$); the positions of the peak being independent of $V_a$ in the double focusing instruments.

If the potential on the relevant electrode is changed by $\Delta V = V_1 - V_2$ so that the peak for $M_2$ will appear at the same position as that for $M_1$, then the resolution can be found from the relation

$$\frac{\Delta M}{M} = \frac{\Delta V}{V}$$

There are various techniques for the precision determination of the matching condition. The earliest of these utilized the exceptional power of the eye to detect the mismatch between the positions of the two peaks. Averaging over a number of successive observations was usually taken to establish the final doublet separation. This is an 'on-line' technique. In more recent work, the technique has been improved by signal averaging method in which the spectral information is stored in a digital memory. The signal averaging technique can also be applied in the case of 'off-line' methods of mass analysis. this exploits the computer analysis of the information stored in the digital memory.

**(II) Quadrupole mass spectrometer**

Quadrupole mass spectrometer was first developed by W. Paul, H. P. Reinhard and U. Von Zahn in Germany in 1950.

In this instrument, the ions travelling in the z-direction enter a two dimensional electric field in which the equipotentials are rectangular hyperbolas of the form (see Appendix AIII)

$$V = (V_0/2r^2)(x^2 - y^2)$$

Such a field can be produced by a set of four symmetrically placed electrodes having the shape of hyperbolas (see Fig. 12.20). The opposite electrodes have potentials of the same sign given by $\pm V_0/2$ the separation between the electrodes being $2r_0$. In practice, the above system of electrodes can be replaced by a set of four circular metallic rods of radius $r = 1.16 r_0$ each to produce a field along the z-axis which closely resembles the field in the actual case.
If a single quadrupole lens is used in which $V_0$ is constant, there is focusing in one plane and defocusing in the other, depending on the signs of the field gradients in the two directions $x$ and $y$.

If however, a sinusoidal rf field is superimposed upon the dc field, the potential $V_0$ can be written as

$$V_0 = U - V \cos \omega t.$$ ...

(8.9-7)

The equation of motion along $x$ and $y$ in this field are

$$\ddot{x} + \left(\frac{q}{M_0^2} \right) (U - V \cos \omega t) x = 0$$

(8.9-8)

and

$$\ddot{y} + \left(\frac{q}{M_0^2} \right) (U - V \cos \omega t) y = 0.$$ ...

(8.9-9)

where we have written

$$a = a_x = -a_y = 4 \frac{qU}{M_0^2 \omega^2}$$ ...

(8.9-10)

$$b = b_x = -b_y = 2 \frac{qV}{M_0^2 \omega^2}.$$ ...

(8.9-11)

and

$$\xi = \omega t/2.$$ ...

(8.9-12)

$u$ is either $x$ or $y$. Eq. (8.9-9) is the well-known Mathieu equation which describes the ion trajectories. The solution for $u$ comes out in a series form, involving terms in $\exp(\mu \xi)^2$. For $\mu$ imaginary, the solution is oscillatory with finite amplitudes while for $\mu$ real, the solution involves hyperbolic functions leading to instabilities in the orbits.

If the rf component is absent, then the equation has the form

$$\ddot{x} + \omega_x^2 x = 0$$

which is oscillatory (for $U > 0$). With a moderate rf component, this oscillatory feature is maintained and there is focusing in the $x-z$ plane. However, since the field has opposite gradient along $y$, there is defocusing in the $y-z$ plane with the d.c. field alone. However, the superposition of a sufficiently large rf field opposes this and makes the motion oscillatory in the $y-z$ plane, so that there is focusing in this plane also. The combination acts as a mass filter.

The mass spectrum is scanned by varying both the dc and rf fields, such that the ratio $U/V$ remains constant, keeping the frequency $\omega$ of the rf field constant.

The resolution can be changed by changing the ratio $U/V = a_x/2b_y$. The limiting values for $a_x$ and $b_y$ obtained by solving the Mathieu equations numerically are $a_x = 0.23699$ and $b_y = 0.70600$. For an instrument with unlimited cross section and length, unlimited resolution seems possible. The practical limit of the resolving power is 8000.

An empirical expression for the resolving power is

$$\frac{M}{\Delta M} = \frac{n^2}{12.2}$$ ...

(8.9-13)

where $n$ is the number of rf cycles in the length $l$ of the analyzer being given by

$$n = \frac{\omega l}{2 \pi} \left( \frac{M}{2E_x} \right)^{1/2}.$$ ...

(8.9-14)

where $E_x$ is the axial energy.

Quadrupole mass spectrometers have the following special features:

(a) small size and weight;
(b) rapid scanning of the mass spectrum;
(c) linear operation up to relatively high pressure ($10^{-4}$ torr); (d) low source energy (10 eV) and (e) electrical variation of the resolving power. The instruments are used in vacuum technology, secondary ion mass spectrometry (SIMS), upper atmospheric and space research.

8.10 Measurement of nuclear spin and magnetic moment; Hyperfine splitting of the atomic energy levels

In Ch. II we introduced the idea of nuclear spin, which is the total nuclear angular momentum given by $I = I_{\text{nuc}} + S_{\text{nuc}}$ and $S$ being the resultant orbital and intrinsic spin angular momenta of the nucleons in the nucleus: $L_{\text{nuc}} = \Sigma L_t$ and $S_{\text{nuc}} = \Sigma S_t$. The summations are over all the nucleons in the nucleus. The above angular momenta are all measured in units of $\hbar$. For even $A$ nuclei, $I$ is an integer while for odd $A$ nuclei, $I$ is half-integral.

The orbital and spin angular momenta of the nuclei are intimately connected with the corresponding magnetic moments ($\mu_L$ and $\mu_S$) while the total nuclear angular momentum $I$ is related to the resultant nuclear magnetic moment $\mu_I$. These have been discussed in Ch. II.

Some of the methods for the measurement of the nuclear spin and magnetic moment are based on observations on the atomic spectral lines. We shall briefly recapitulate the salient points about the latter which were discussed fully in Vol. I.

The atomic energy levels are characterized by the quantum numbers $L$ ($= L_t$), $S$ ($= S_t$) and $J$ ($= J_t$) of the orbital electrons. The resultant atomic angular momentum $J$ is the vector sum of $L$ and $S$: $J = L + S$. Because of the magnetic interaction between the magnetic moments $\mu_L$ due to the orbital motion and $\mu_S$ due to the spin motion of the electrons, an atomic energy level with given values of $L$ and $S$ splits into a number of sublevels with different values of $J$, where $J$ can take up the values

$$L - S, L - S + 1, L - S + 2, \ldots, (L + S).$$

For $L > S$ the number of sublevels of different $J$ is $(2S + 1)$ while for $L < S$ it is $(2L + 1)$. The splitting of the levels can be calculated with the help of quantum mechanics. The expression for the splitting is of the form

$$\Delta E = \langle f(r) \rangle > L \cdot S$$ ...

(8.10-1)
where \( <f(r)> \) is the expectation value of the operator \( f(r) \) given by

\[
f(r) = -\frac{e}{2m_e^2 c^2} \frac{1}{r} \left( \frac{\partial V}{\partial r} \right)
\]...

\((8.10-2)\)

\( <f(r)> \) is calculated by using the radial part of the uncorrected wave function. \( V = V(r) \) is the spherically symmetric central potential acting on the electron. The expression for \( \Delta E \) shows the explicit dependence of the spin-orbit energy on the relative orientations of \( L \) and \( S \).

The splitting of the atomic energy levels due to spin-orbit interaction is known as the fine-structure splitting. The transitions between the split levels in two states of given \( L \) values (governed by the selection rule \( \Delta L = \pm 1 \)) produce the fine structure of the spectral lines. The transitions take place between the levels of different \( J \) values for the two states governed by the selection rule \( \Delta J = 0, \pm 1 \). A well-known example is the appearance of the two sodium D-lines corresponding to the transitions \( 3^2P_{1/2} \rightarrow 3^2S_{1/2}(D_1) \) and \( 3^2P_{3/2} \rightarrow 3^2S_{1/2}(D_2) \) due to the fine structure splitting in the transition \( 3P \rightarrow 3S \).

Hyperfine splitting:
Apart from the electronic angular momenta \( L \) and \( S \), the atom also possesses the nuclear angular momentum \( I \). Hence the total angular momentum of the atom is

\[
F = L + S + I = J + I
\]...

\((8.10-3)\)

The possible values of \( F \) are \( |J - I|, \ldots (J + I) \). Thus if \( J < I \), the number of possible values of \( F \) is \( 2(J + 1) \) while for \( J > I \), this number is \( 2(I + 1) \). The levels of the same \( J \) and \( I \) having different values of \( F \) have slightly different energies. Thus a level of given \( J \) and \( I \) values splits up into sublevels of different \( F \). The transitions between the levels with different \( F \)-values in the upper and lower states (of definite \( J, I \) values) give rise to the hyperfine structure of the spectral lines. An example is shown in Fig. 8.15 for the sodium D\(_1\) line, for which the upper and lower states have \( J = 3/2, I = 3/2 \) and \( J = 1/2, I = 3/2 \) respectively, the nuclear spin of \(^{23}\)Na being \( I = 3/2 \). Thus the possible \( F \) values for the upper state are \( F = 0, 1, 2, 3 \) while those for the lower state are \( F = 1, 2, 3 \).

The selection rules governing the transitions are

\[
\Delta F = 0, \pm 1
\]
\[
\Delta J = 0, \pm 1, \Delta L = \pm 1
\]...

\((8.10-4)\)

\( \Delta F = 0, \pm 1 \), \( \Delta J = 0, \pm 1, \Delta L = \pm 1 \)

\( \Delta J = 0, \pm 1, \Delta L = \pm 1 \)

Fig. 8.15 Origin of hyperfine structure of sodium D\(_1\) line.

**Determination of Some Nuclear Properties**

The splitting between the levels of different \( F \) values in a state of given \( J \) and \( I \) is given by a formula similar to Eq. (8.10-1).

The interaction energy \( \Delta U \) between the magnetic moment \( \mu \) of the nucleus and the magnetic induction field \( B_\| \) at the nucleus due to the resultant electronic magnetic moment is given by

\[
\Delta U = -\mu \cdot B_\|
\]...

\((8.10-6)\)

We have to take the time averaged value \( <\Delta U> \) which depends on the time averaged value of the magnetic field \( B_\| \) at the nucleus. Thus the time averaged field \( B_\| \) is in the direction of the total electronic magnetic moment parallel to \( J \), the component of \( \mu \) perpendicular to \( J \) averaging out to zero; (see Ch. VI, Vol. I). Hence we can write

\[
<\mu \cdot B> = -a J/J
\]...

\((8.10-7)\)

where \( a \) is a constant.

The nuclear magnetic moment \( \mu \) is parallel to the nuclear spin \( I \) and is given by

\[
\mu = g_I \mu_N I
\]...

\((8.10-8)\)

This can be written as

\[
\mu = g_I I / I
\]...

\((8.10-9)\)

\( \mu \) is the nuclear magneton, \( g_I \) is the nuclear \( g \)-factor. The quantum mechanical value of the nuclear spin is \( \sqrt{I(I+1)} \hbar \). The interaction energy is then

\[
\Delta U = a \mu, (I \cdot J) / I J
\]...

\((8.10-10)\)

Eq. (8.10-3) can be used to find the scalar product \( I \cdot J \). Using the quantum mechanical values of the angular momenta we get

\[
2 I \cdot J = F(F+1) - I(I+1) - J(J+1)
\]

so that

\[
\Delta U = a \mu, F(F+1) - I(I+1) - J(J+1) / 2 \sqrt{J(J+1) \cdot I(I+1)}
\]...

\((8.10-11)\)

Since the hyperfine splitting depends on the nuclear magnetic moment \( \mu \), which is three orders of magnitude smaller than the atomic magnetic moment, the hyperfine splitting is much smaller than the fine structure splitting.

Eq. (8.10-11) can be written as

\[
\Delta U = \frac{1}{2} \hbar \Delta v_0 (F(F+1) - I(I+1) - J(J+1))
\]

where \( \Delta v_0 \) is known as the h.f.s. separation constant.

The constant \( a \) in Eq. (8.10-11) must be calculated for each atomic configuration. For given \( J \) and \( I \), the interaction energy \( \Delta U \) has the same number of values as \( F \).

Eq. (8.10-11) shows that it is possible to determine the nuclear spin by one of the following three methods.

(a) If \( J > I \) the number of lines due to hyperfine splitting is equal to \( (2I + 1) \) provided the hyperfine splitting of one of the states involved in
the transition is negligibly small compared to the other, so that the nuclear
spin can be determined by counting the number of hyperfine lines for a
completely resolved spectrum. As an example, for praseodymium, all the
resolved lines are found to have six components. In all cases $J$ is known
to be large ($J > I$). Hence $I = 5/2$ for Pr.

(b) If however $J < I$, we can determine $I$ by using a rule known as
the interval rule. The energy difference between two states $F$ and $(F - 1)$
given $J$ and $I$ is given by

$$
\delta(\Delta U) = \frac{a \mu_I}{2} \frac{F(F+1) - (F-1)F}{\sqrt{J(J+1)} \cdot \sqrt{I(I+1)}}
$$

This interval $\delta(\Delta U)$ is known as the hyperfine splitting (h.f.s.). The ratio
of the splittings between adjacent levels $F$, $F - 1$, $F - 2$, etc., $(F = J + I)$
is thus

$$
\delta(\Delta U)_F : \delta(\Delta U)_{F-1} : \delta(\Delta U)_{F-2} : \cdots = F : F-1 : F-2 : \cdots = (J+I) : (J+I-1) : (J+I-2) : \cdots
$$

(c) In some cases neither of the above methods is applicable. If in such
a case, the hyperfine splitting of the sublevels in one of the states of given
$J$ and $I$ is very small (usually the upper state), then the hyperfine structure of
the spectral line corresponds to that of the lower state. Thus for the two
sodium D-lines the splitting of the lower state $3^2\text{S}_{1/2}$ $(F = 1, 2)$ is much
greater than that of the upper state for each. The latter are $3^2\text{P}_{3/2}$ for $D_1$ $(F = 1, 2)$ and $3^2\text{P}_{1/2}$ for $D_2$ $(F = 0, 1, 2, 3)$. So each of these lines splits into
two hyperfine components with $\Delta \lambda_1 = 0.021 \text{ Å}$ and $\Delta \lambda_2 = 0.023 \text{ Å}$ for both.

In such cases $I$ can be determined by comparing the intensities of the
components of the hyperfine splitting. The intensity of a spectral line is
proportional to $(2F + 1)$ which is equal to the number into which a level
splits in an external magnetic field (see later).

The constant $a$ appearing in Eq. (8.10-11) depends on the magnetic
field due to the electrons at the nucleus. This can be determined
accurately only in very few cases (of the simplest atomic, systems), e.g.,
hydrogen, hydrogen-like atoms, halogens and alkaline earth elements.
This field is $\sim 10$ to $100$ T. In general $a$ cannot be calculated with an error
less than 10%. Hence nuclear magnetic moment determined from h.f.s.
studies are not very accurate. It is found that for $\mu_1 > 0$, a sublevel of
higher $F$ lies above one of lower $F$.

The magnetic moment of the nucleus $\mu_1$ can be determined from
hyperfine structure by a measurement of the h.f.s. splitting which yields
the value of $a$ appearing in Eq. (8.10-10), provided the nuclear spin $I$
is known. $\mu_1$ determined by this method is not very accurate. The sign of $\mu_1$
(+ or -) can also be determined by noting whether the term order is

\[ \Delta E_B = - \left( \frac{\mu_J}{J} \cdot J \cdot B + \frac{\mu_I}{I} \cdot I \cdot B \right) \]
Since \( \mu_I < < \mu_J \), the second term can be neglected. \( \Delta E_B \) then comes out to be (see Nuclear Moments and Statistics by N.F. Ramsay in Experimental Nuclear Physics, Vol. I, Ed. E. Segre).

\[
\Delta E_B = \frac{\mu_I - F (F + 1) + J (J + 1) - I (I + 1)}{2F (F + 1)} BM_F \quad (8.11-2)
\]

The magnitude of the splitting actually depends upon \( \mu_F \) which is of the same order as \( \mu_J \).

Eq. (8.11-1) shows that each state of a given \( F \) splits up into \( (2F + 1) \) levels of different \( M_F \). The states of different \( M_F \) are equidistant. The splitting increases with increasing \( B \). The selection rules for the transition between states of different \( M_F \) in the upper and lower \( F \) states are

\[
\Delta M_F = 0, \pm 1 \quad (\text{for } M_F = 0 \text{ to } M_F = 0).
\]

These are similar to the selection rules for \( M_J \) for ordinary anomalous Zeeman effect, as discussed in Ch. VI in Vol. I. Thus the Zeeman-patterns in the two cases are very similar.

The case discussed above is known as the weak field case. It gives rise to a pattern similar to the anomalous Zeeman pattern in the electronic spectrum of the atom.

**b) Strong field case**

This corresponds to Paschen-Back effect discussed in the case of magnetic splitting of the atomic spectral lines, discussed in Ch. VI, Vol. I. The coupling between \( J \) and \( I \) is broken by the action of the magnetic field \( B \) and they precess independently about the latter, as shown in Fig. 8.16 on the right side.

The possible orientations of \( J \) in the magnetic field, following the rules of space quantization gives the following \( (2J + 1) \) values of the components \( M_J \) of \( J \) along \( B \):

\[
M_J = J, J - 1, J - 2 \ldots - J
\]

Similarly the following \( (2I + 1) \) values of the components \( M_I \) of the vector \( I \) in the field direction are possible:

\[
M_I = I, I - 1, I - 2 \ldots - I
\]

Each of these component levels has a different energy due to the interaction with the magnetic field given by

\[
\Delta E_J = -\frac{\mu_J}{J} J \cdot B = -\mu_J BM_J / J \]

\[
\Delta E_I = -\frac{\mu_I}{I} I \cdot B = -\mu_I BM_I / I
\]

Since \( \mu_I < < \mu_J \), the main contribution to the level-splitting is from the term \( \Delta E_J \). The separation between the adjacent levels of different \( M_J \) is \( \mu_J B / J \). Each of these levels of definite \( M_J \) splits up into \( 2J + 1 \) sub-levels determined by \( \Delta E_I \), the separation between the adjacent levels \( \mu_I B / I \) being small compared to that between the \( M_J \) levels, as illustrated in Fig. 8.17 for \( I = 3/2 \). The nuclear spin \( I \) can be determined from the number \( (2I + 1) \) sublevels of different \( M_F \).

It may be noted that the total number of sublevels into which the hyperfine levels of given \( J \) and \( I \) split is the same for both the weak field case and the strong field case. As an example, for \( J = 1/2 \) and \( I = 3/2 \), the possible \( F \) values in the weak field case are \( F = 3 \) and \( 1 \). The number of sublevels into which these split in the magnetic field are \( (2 \times 3 + 1) = 7 \) and \( (2 \times 1 + 1) = 3 \) respectively, the total being 8. In the strong field the number of sublevels is \( (2J + 1)(2I + 1) = (2 \times 1 + 1) \times (2 \times 3 + 1) = 2 \times 4 = 8 \).

In Fig. 8.18 is shown the splitting of the two h.f.s. components in a weak field on the left for the above values of \( J \) and \( I \). The ordering of the sublevels is reversed in the lower state, because \( J \) is antiparallel to \( I \) for it. The transition to the strong field case is shown on the right.

**Isotope effect**

Apart from the h.f.s. splitting, discussed above, the atomic spectral lines are found to undergo another type of splitting, known as isotope shift. Though this has nothing to do with the nuclear spin we include a brief discussion about it here since the two effects are of the same order of magnitude and are often present simultaneously. Many chemical elements have a number of isotopic atoms which have different atomic masses though they have the same number of extra-nuclear electrons. Because of the simultaneous motion of the electrons and the nucleus (of
finite mass) about the common centre of mass, the atomic states have slightly different energies for the different isotopes, even though they may have the same set of quantum numbers. A well-known case is the atomic states of the deuterium atom with \( A = 2 \), which differ slightly in energy from the corresponding states of the hydrogen atom with \( A = 1 \). The Rydberg constants differ slightly in the two cases which causes the spectral lines to differ in wavelength by a small amount for the two isotopes. It was this difference which led to the discovery of deuterium (heavy hydrogen) by H.C. Urey and his co-workers, which was discussed in detail in Ch. IV of Vol. I.

In the case of complex atoms, the change of energy of the levels due to different isotopic masses cannot be calculated easily. Since the different stable isotopes of an element are always present with the same relative abundance in the natural state of the element, the spectral lines due to the different isotopes are observed as companion lines with small separations between them. The separations are usually of the same order of magnitude as the separation between the hyperfine spectral lines of the element. It is not easy to separate the two effects (isotopic effect and the nuclear spin effect). Comparison of the intensities of the components gives some information in some cases. For example the 6215Å line of zinc (Z = 30) shows three close lying components due to the three isotopes \(^{64}\text{Zn} \), \(^{66}\text{Zn} \) and \(^{68}\text{Zn} \) whose intensities correspond to the known relative abundances of these isotopes in natural zinc. The frequency difference between the lines are proportional to the isotopic mass differences. Since these are all even-even nuclei, the nuclear spin \( I = 0 \) for all of them so that the lines are not expected to have h.f.s. structure. An unambiguous interpretation is possible from the study of the Zeeman patterns of the components. In the case of simple isotopic effect, the lines of the different isotopes will show the Zeeman effect for the extra-nuclear electrons independently of one another. On the other hand, h.f.s. components due to nuclear spin show different kinds of Zeeman pattern (see later).

In the case of lighter elements, the isotopic effect is due to the different masses of the different isotopic atoms. For the heavier elements the effect is mainly due to the differences in the nuclear radii which depend on the isotopic masses \((R \propto A^{1/3})\).

In the case of elements with both even and odd \( A \) stable isotopes, both isotopic effect and h.f.s. splitting are present which makes the analysis very difficult.

8.12 Nuclear spin and statistics from molecular spectra

In this method, the nuclear spin is determined from the measurement of the alternation of the intensities of the lines in the band spectrum of homonuclear diatomic molecules such as \(^{H_2} \), \(^{O_2} \) etc.

As we saw in Ch. XIII, Vol. I, the energies of the molecular levels are determined by the rotational, vibrational and electronic states of the molecule. Pure rotational bands appear due to the transitions between the rotational levels of the molecule without change of vibrational or electronic states and lie in the far infra-red. Rotation-vibration bands appear when the transitions take place between the rotational levels belonging to different vibrational states without any change in the electronic state. They lie in the near infra-red. Finally, if all the three states are changed, electronic bands appear which lie in the visible or ultraviolet region.

The total wave function of a diatomic molecule can be written approximately as the product of the wave functions \( \psi_r \), \( \psi_v \), and \( \psi_e \) of the nuclei of the two atoms comprising the molecule (Born–Oppenheimer approximation): \( \psi = \psi_r \psi_v \psi_e \).

The symmetry characteristics of the total wave function \( \psi \) are determined by the symmetries of the four component wave functions. These symmetry characteristics determine the nature of the statistics obeyed by the particles constituting the system. Thus, in a homonuclear diatomic molecule, if the total wave function changes sign on interchange of all the coordinates (space plus spin) of the two constituent nuclei, then these nuclei are said to obey Fermi-Dirac statistics. On the other hand, if the total wave function remains unchanged on interchange of all the coordinates of the constituent nuclei, then the two nuclei are said to obey Bose-Einstein statistics (see Ch. XVII Vol. I). Denoting all the space coordinates by \( r \) and the spin coordinates by \( \sigma \) we have for the diatomic molecule

\[
\psi(r_1, r_2, \sigma_1, \sigma_2) = -\psi(r_2, r_1, \sigma_2, \sigma_1) \quad \text{(Fermi-Dirac)}
\]

\[
\psi(r_1, r_2, \sigma_1, \sigma_2) = \psi(r_2, r_1, \sigma_1, \sigma_2) \quad \text{(Bose-Einstein)}
\]

Here the suffixes 1 and 2 refer to the two nuclei. Let us now examine the symmetries of the space and spin wave functions.

Interchanging the nuclei may or may not result in a change of the sign of \( \psi \). In the first case we have an antisymmetric electronic wave function. In the second case it is symmetric. In general \( \psi_e \) is symmetric in the ground state of the molecule. The vibrational wave function is symmetric for all states.

The rotational wave function \( \psi_r \) involves the spherical harmonics and is symmetric if the rotational quantum number \( J \) is even and antisymmetric if \( J \) is odd. For a diatomic homonuclear molecule, e.g., \(^{H_2} \), \(^{N_2} \), \(^{O_2} \) etc. the rotational energy is

\[
E_r = \frac{J(J+1) \hbar^2}{2K}
\]

where \( K \) = moment of inertia of the molecule. The spacings between the consecutive levels is given by

\[
\Delta E_r = \frac{\hbar^2}{2K} \left[ J(J+1) - (J-1) \right] J = \frac{\hbar^2 J}{K}
\]

Thus \( \Delta E_r \propto J \). This is shown in Fig. 8.19.
Finally the symmetry of the spin function depends on the total nuclear spin of the molecule given by $S = I_1 + I_2$ where $I_1$ and $I_2$ are the spin vectors of the two nuclei. In the present case $I_1 = I_2 = I$ (say).

For a nucleus of spin $I$ there are $(2I + 1)$ substates with the magnetic quantum numbers $M = I, \bar{I} - 1, \ldots, -I$. This is true for each nucleus in the molecule. If $\chi^M_I$ denotes the spin function of the nucleus the total spin wave function is of the form

$$\chi^M_n = \chi^M_I \chi^M_I = \chi^M_I \chi^M_{I'} = \chi^M_I \chi^M_{I'}$$

If we have two identical nuclei the spin wave function on interchanging the spin orientations of the two nuclei becomes

$$\chi^M_{n'} = \chi^M_{I'} \chi^M_{I'} = \chi^M_{I'} \chi^M_{I'}$$

In this case the spin wave function of the molecule is a linear combination of the above two and can be either symmetric or antisymmetric:

$$\chi^M_{n2} = \chi^M_I \chi^M_I (2) + \chi^M_I \chi^M_I (1)$$

The number of these functions is $(2I + 1)^2$. Out of these, there are $2I + 1$ symmetric functions corresponding to $M = M'$ of the form $\chi^M_I (1) \chi^M_{I'} (2)$. The antisymmetric combination vanishes in this case. Of the remaining $(2I + 1)^2 - (2I + 1) = 2I (2I + 1)$ functions, half are symmetric and half are antisymmetric. Thus we have:

- No. of symmetric spin functions: $(2I + 1) (2I + 1)$
- No. of antisymmetric spin functions: $I (2I + 1)$

So the ratio of the number of symmetric to antisymmetric spin functions is

$$r = \frac{(I + 1)}{I}$$

We have seen above that for diatomic molecules, the alternate rotational states with even and odd $J$ are symmetric and antisymmetric. So they have to be combined with the antisymmetric and symmetric spin functions respectively if the nuclei obey F-D statistics. For nuclei obeying B-E statistics, the converse is true. This assumes that the electronic states are symmetric.

The above considerations show that the alternate rotational levels of the diatomic molecules have statistical weights in the ratio $(I + 1)/I$. Hence the alternate rotational lines have intensities in the ratio of $(I + 1):I$. In terms of the $J$-value of the initial states we can then write:

- For nuclei obeying B-E statistics: $J$ (even lines) $J$ (odd lines) = $(I + 1)/I$. Thus the $J$-even lines are stronger.
- For nuclei obeying F-D statistics: $J$ (odd lines) $J$ (even lines) = $(I + 1)/I$. So the $J$-odd lines are stronger.

For nuclei obeying F-D statistics, the ratio $r = \infty$ which means that the odd rotational lines will be missing. This is actually found to be the case, which confirms the above assignment of the spin value and statistics to $^{16}O$.

Actually diatomic homonuclear molecules do not show pure rotational or pure rotation-vibration spectra (see § 13.3, Vol. I). The selection rule $\Delta J = \pm 1$ would require transition between symmetric and antisymmetric states in dipole transitions. Such transitions are very improbable. However, the restriction is removed in the case of electronic bands, many of which show the transitions with $\Delta J = 0, \pm 1$. In such bands, the alternate rotational lines are found to have intensity ratios obeying the above law.

8.13 Atomic beam method of nuclear magnetic moment determination (non-resonance method)

This method is similar to Stern and Gerlach's method of determining the atomic magnetic moments by producing deflection of a neutral atomic beam in a highly inhomogeneous magnetic field. The method was discussed in detail in Ch. VI, Vol. I.

If the magnetic induction field $B$ and its gradient are both along the $z$-axis, then the translatory force on an atom with a magnetic moment $\mu$ is

$$F = \mu_z \frac{\partial B}{\partial z} \tag{8.13-1}$$

where $\mu.z$ is the $z$-component of the magnetic moment. In the case of the atomic magnetic moment $\mu = g_\mu B / \sqrt{J(J + 1)}$. The above expression for the force reduces to

$$F = g_\mu B M_J \frac{\partial B}{\partial z} \tag{8.13-2}$$

where $J$ is the resultant atomic angular momentum and $M_J$ is the magnetic quantum number with $(2J + 1)$ possible values $J, J - 1, \ldots, -J$. $g_\mu$ is the Landé splitting factor and $\mu_B$ is the Bohr magneton. Since the force depends on $M_J$, the incident beam splits up into $(2J + 1)$ components in the inhomogeneous magnetic field.

The effect is much less in the case of nuclear magnetic moment which is about $10^3$ times less than the atomic magnetic moment. Hence much higher field gradient is needed to produce an observable split in the
beam. Field gradients of the order of $10^3$ T/m or more are needed in this case compared to only about 10 T/m in the case of atomic magnetic moment measurement.

The situation is further complicated due to the presence of the much larger effect due to the atomic magnetic moment. To circumvent this problem, measurements are usually made on molecules with mutually compensated electronic magnetic moments (e.g., H$_2$, H$_2$O etc.).

O. Stern, I. Estermann and R. Frisch have used this method to measure the magnetic moment of the proton, which was found to be about 2.5 $\mu_N$.

The method is not an accurate one and several new methods have since been developed for measuring the nuclear magnetic moments very accurately (see later).

In a variation of the method, a weak magnetic field is used such that the coupling between $I$ and $J$ is preserved to produce the resultant $F$ which splits up into $(2F+1)$ components. These can be counted to yield the value of $F$ from which $I$ can be found if $J$ is known. The method gives the nuclear spin, but not the nuclear magnetic moment.

### 8.14 Magnetic resonance method of Rabi

This is a fairly accurate method for determining the nuclear magnetic moment and was developed by I.I. Rabi and his colleagues (1939). The method involves reorientation of the nuclear spin $I$ and the nuclear magnetic moment by a resonance high frequency electromagnetic field and the calculation of $\mu_I$ from the resonance frequency $\nu_{\text{res}}$.

![Image of Rabi's molecular beam magnetic resonance method](image)

**Fig. 8.20. Rabi's molecular beam magnetic resonance method of determining nuclear magnetic moment.**

The apparatus used by Rabi is shown schematically in Fig. 8.20. Rabi and his colleagues determined $\mu_I$ for the nucleus $^6$Li in their first experiment. LiCl was used as the experimental substance which was evaporated in the oven O. LiCl molecules escaped through an orifice on the wall of O and entered the highly inhomogeneous magnetic field ($\sim 10^3$ T/m) between the specially shaped pole-pieces of the magnet A (see Ch. VI, Vol. I). $S$ was the defining slit at the exit end of the magnet A. The detector D was a hot tungsten wire (1 mil in diameter). A neutral alkali atom striking its surface delivers its valence electron to the wire and the positive ion is boiled off. The current to the wire is a measure of the intensity of the LiCl beam falling on the detector.

The beam passes through the three magnets A, B and C. The magnets A and C are identical in all respects except that the inhomogeneities are in opposite directions (+ z and − z) in them. The fields in both of them point upwards (+ z) and are very high (−1.2 T). The translatory force acting on the magnetic dipoles of moment $\mu_I$ in each is

$$F = \mu_I \frac{\partial B}{\partial z} = g_I \mu_N M_I \frac{\partial B}{\partial z}$$  \hspace{1cm} (8.14-1)

Here $g_I$ is the nuclear $g$-factor and $M_I$ can have the $(2I + 1)$ values given by $M_I = I, I - 1, I - 2, \ldots - I$.

Due to this force, the molecular dipoles are deflected in going through A. Those emitted in a certain definite direction follow the trajectory as shown in Fig. 8.21.

![Image of trajectory](image)

**Fig. 8.21. Trajectory of a molecular dipole in an inhomogeneous magnetic field.**

Because of the difference in the force acting on the nuclear magnetic moment $\mu_I$ in the inhomogenous magnetic field in A determined by the different possible values of $M_I$ in Eq. (8.14-1), the molecular beam splits up into $(2I + 1)$ different beams after emerging from A. In the present case since $I = 3/2$ for $^6$Li nucleus, the beam splits up into four, the possible values of $M_I$ being $+3/2, +1/2, -1/2$ and $-3/2$.

After going through the region B, they are deflected in the opposite direction in C and are refocused on the detector D because of the equal and opposite force experienced by them in C, provided that the orientation of their magnetic dipole moment remains unchanged.

The magnet B produces a homogenous and steady magnetic field $B_0$ along z. The magnetic moments of the molecules precess about it. The alignment of $M_I$ w.r.t. $B_0$ is determined by the rules of space quantization.

The energy of the dipole in the magnetic field $B_0$ is given by

$$\Delta U_m = - \mu_I \cdot B_0 = - g_I \mu_N M_I B_0$$  \hspace{1cm} (8.14-2)

The energy difference between the successive states of different orientations of $\mu_I$ is thus

$$\delta (\Delta U_m) = g_I \mu_N B_0 = \frac{eB_0}{2M_p} = \hbar \omega_L$$  \hspace{1cm} (8.14-3)

where

$$\omega_L = \frac{eB_0}{2M_p}$$  \hspace{1cm} (8.14-4)

$\omega_L$ is the Larmor precessional frequency.
If now a sinusoidal magnetic field is produced in the same region as B at right angles to the steady field \(B_0\), it can induce transition from one magnetic substate of the nuclear dipole of \(^7\)Li nucleus to another, provided the frequency of the sinusoidal field becomes equal to the Larmor frequency \(\omega_L\). The sinusoidal field is produced by passing an alternating current through a hairpin loop from an rf oscillator.

When the resonance transition takes place, the LiCl molecules can no longer be refocused by the inhomogenous field in C onto the detector D due to the change of orientation of the nuclear magnetic moment of \(^7\)Li nucleus. Thus, there is a sudden drop in the detector current when the circular frequency \(\omega\) of the applied rf field becomes equal to the Larmor frequency \(\omega_L\).

It has been assumed above that the magnetic nuclear moment \(\mu_1\) of \(^7\)Li interacts with the external magnetic field only. This is possible because the electronic magnetic moment of LiCl molecule in the ground state is zero. Further, it is assumed that the magnetic interaction between \(\mu_1\) (\(^7\)Li) with the fields due to the nuclear magnetic moment of the Cl atom and due to the rotational angular momentum of the LiCl molecule are so weak that these can be neglected.

From the resonance condition
\[
\omega = \omega_L = g_I (2B_0/2M_p) \quad (8.14-5)
\]
the value of \(g_I\) can be determined which yields the value of \(\mu_1\).

Rabi calculated the quantum mechanical probability of transition for \(I = 1/2\) between two different \(M_I\) states \((M_I = \pm 1/2)\) which is given by
\[
P_{1/2,-1/2} = \sin^2 \frac{1}{2 \sqrt{2}} \left(1 - r^2 + \Delta^2\right)^{1/2} \quad (8.14-6)
\]
where \(r = \omega/\omega_L\) and \(\Delta = \tilde{B}/2B_0\). \(\tilde{B}\) is the amplitude of the rf field. \(t\) is the time for which the perturbation acts. At the resonance (\(\omega = \omega_L\)), \(r = 1\). So in this case \(P\) is large, even if \(\Delta\) is small \((\tilde{B} \ll B_0)\), \(P\) has a maximum at the resonance.

Experimentally, the resonance condition is achieved either by changing the frequency \(v = \omega/2\pi\) of the rf field, holding \(B_0\) constant or more commonly by changing \(B_0\) with a constant \(v\).

For \(^7\)Li, Rabi obtained the resonance at \(B_0 = 0.3385\) T for a frequency \(v_L = 5.585\) MHz. Then Eq. (8.14-5) gives for \(^7\)Li
\[
\omega_L = \frac{\hbar}{eB_0/2M_p} = \frac{\hbar}{\mu_0 B_0} \quad (8.14-7)
\]
\[
= \frac{6.6262 \times 10^{-34} \times 5.585 \times 10^6}{0.3385 \times 5.0508 \times 10^{-23}}
\]
\[
= 2.161
\]

Then the nuclear spin of \(^7\)Li comes out to be \(M_I = g_I = 2.161 \times 3/2 = 3.242\) in nuclear magneton.

The expression for \(P\) has been extended by Majorana to any arbitrary spin \(I\) (see Nuclear Moments and Statistics by N.F. Ramsey in Experimental Nuclear Physics, Vol. I, Ed. E. Segre).

Fig. 8.22 shows a typical resonance curve for \(^7\)Li nuclear magnetic moment measurement.

Rabi's method for the determination of the magnetic moment of nuclei was used by L.W. Alvarez and F. Bloch in a modified form to determine the magnetic moment of the neutron (see § 13.2).

### 8.15 Magnetic resonance absorption method of measuring nuclear magnetic moment

In this method developed by E.M. Purcell, H.C. Torrey and R.V. Pound (1946), the reorientation of the nuclear magnetic moment in a steady magnetic field due to an oscillating weak magnetic field is determined by the absorption of radiation from an rf oscillator under resonance condition. They first observed the resonance effect in solids. Later the method was extended to liquids and gases.

The orientation of the nuclear magnetic moment is associated with the change of the magnetic energy. For example, in the case of protons \((I = 1/2)\), the two magnetic states correspond to \(m = +1/2\) and \(m = -1/2\). The magnetic energy change in a steady magnetic field \(B_0\), between these two states is
\[
\Delta U_m = \mu_p B_0 - (-\mu_p B_0) = 2\mu_p B_0 \quad (8.15-1)
\]

The transition is induced by an oscillating magnetic field having frequency equal to the Larmor frequency of precession in the steady field as in Rabi's molecular beam experiment determined by Eq. (8.14-5).

Considering the case of protons (in a sample of some hydrogenous material, such as paraffin), the induced transition will be from the lower to the higher energy state (absorption) or from the higher to the lower energy state (stimulated emission).

Though the absorption of radiation is largely cancelled by stimulated emission, they do not completely cancel one another. In fact because of the larger population \((n_1)\) of the protons in the lower energy state compared to that in higher energy state \((n_2)\) as determined by Maxwell-Boltzmann statistics, there is slight preponderance of the absorption process over the stimulated emission process. The ratio
\[
\frac{n_2}{n_1} = \exp(-\Delta U/k T) \quad (8.15-2)
\]
For a magnetic induction field $B_0 = 0.7 \, \text{T}$, the transition energy is

$$
\Delta U = 2 \mu_p B_0 = 2 \times 2.7927 \mu_N \times 0.7
$$

where

$$
\mu_N = 5.05 \times 10^{-27} \, \text{J/T}
$$

$$
\Delta U = 2 \times 10^{-26} \, \text{J}
$$

At room temperature (300 K), $kT = 4.14 \times 10^{-21} \, \text{J}$.

This shows that $\Delta U < kT$. So we can write

$$
\exp \left( \frac{-\Delta U}{kT} \right) = 1 - \frac{\Delta U}{kT}
$$

Because of the slight preponderance of absorption over stimulated emission, there will be net drawal of energy by the system from the rf source.

In the absence of the external magnetic field, the spins of the protons within the solid are oriented at random. As the field is applied, they try to assume the quantized positions of different $m$ values which affect the ratio $n_2/n_1$, given above. However, because of the thermal motion of the atoms in the lattice, there will be fluctuating motion of the protons, which produces a fluctuating (internal) magnetic field. This will affect the orientation of the spins of the protons in the external field. The interaction of the nuclei with the atomic dipoles results in small shifts of the resonance peaks which depends on the atomic environment and are known as chemical shifts. F. Bloch has developed a method for taking these interactions into account in terms of spin-lattice relaxation times which determine the exponential decay times of the different components of the magnetization to assume equilibrium values. The relaxation times may vary between $10^{-4}$ to $10^2 \, \text{s}$.

The spin-lattice relaxation process occurs due to the sharing of the excess spin energy in the upper state with the surroundings (lattice) due to the vibrations of the latter or to other types of thermal motion (e.g., in liquids and gases). There is also the alternative process of spin-spin relaxation in which the excess energy is shared directly between the nuclei. The relaxation times determine the widths of the N.M.R. peaks which may be quite small ($\sim 0.1 \, \text{Hz}$) as in liquids and gases or fairly large ($\sim 10^3 \, \text{Hz}$) as in solids.

Fig. 8.23 shows a schematic diagram of the apparatus used by Purcell and others.

The sample (pure water) is placed within the rf coil, which is placed in the steady magnetic field, the oscillating field being perpendicular to the steady field. An exactly similar sample is placed in an identical coil (dummy) which however is not placed in the magnetic field. RF power is fed into both coils.

Before the steady field $B_0$ is switched on, the wave forms from the two coils at the input of the receiver are identical. By introducing a phase difference of $180^\circ$, they can be made to cancel one another, as shown by the detector and the oscilloscope.

When $B_0$ is switched on and resonance is achieved, the signal from the sample is attenuated with respect to the dummy and its phase is also changed which shows up as a sharp peak on the oscilloscope trace.

In practice, $B_0$ is modulated by a 30 c.p.s. oscillating current passed through a suitably located coil. A wave form synchronous with this is applied to the horizontal plates of the oscilloscope which yields the pattern as shown in Fig. 8.24.

The nuclear magnetic resonance (N.M.R.) method is one of the most accurate methods of measuring the magnetic moments of nuclei. The accuracy is determined by the accuracy with which the steady field $B_0$ and the oscillator frequency can be measured. Highly precision methods have been developed for their measurements and the accuracies achievable in the measurement of $\mu_N$ by this method is better than 1 part in $10^6$. In fact, these constitute one of the most accurate measurements in physics.

The N.M.R. method can be used in monitoring a steady magnetic field. It is helpful in the analysis of the structure of liquids, dielectric crystals, metals, semiconductors and polymers.

The value of the proton magnetic moment determined by this method recently is

$$
\mu_p = 2.792845 \mu_N
$$

Electron paramagnetic resonance :

A method closely similar to the nuclear magnetic resonance method discussed above is the electron paramagnetic resonance (EPR) method first introduced by E. Zavoisky. Because of the much larger value of the
electronic magnetic moment, the splitting between the adjacent levels of different magnetic quantum numbers is much larger in this case for the same magnetic field. The resonance frequency is correspondingly much higher, being of the order of several thousand MHz, compared to a few MHz for the nuclear magnetic resonance. These frequencies are in the microwave range.

In the EPR experiments, the frequency is kept fixed and the magnetic field is varied to obtain resonance, while in NMR experiment, the procedure is just the opposite.

In many solids the paramagnetic ions behave as if they had a single electron. Hence there are only two magnetic substates with $m_s = \pm \frac{1}{2}$ which have different energies in an external magnetic field. When the frequency of the rf field is equal to the Larmor frequency (resonance), transition will be induced between the two states, which is observed as a dip in the power level of the rf oscillator. Because of the nuclear spin, each of the above magnetic states is split up into $(2i+1)$ closely spaced substates of different $M_f$. This will cause a number of close lying dips to appear in the rf power level as the frequency is varied for a given magnetic field. By counting the number of dips, it is possible to determine the nuclear spin.

### 8.16 Nuclear induction method

This method is similar to the resonance absorption method discussed in the previous section. It was developed by F. Bloch, W.W. Hansen and E. Purcell.

In many linear and symmetric top molecules, the transition energies between some rotational levels lie in the microwave region. If there is a nuclear electric quadrupole interaction within the molecule which affects the rotational energies, then the nuclear spin and the strength of the nuclear quadrupole interaction can be estimated from the analysis of the microwave spectra (see § 8.17).

In some cases the interaction causing the hyperfine splitting in the microwave spectra is magnetic in origin, such as the interaction between the nuclear magnetic moment and the magnetic field due to the electronic motion at the nucleus. In this case the nuclear magnetic moment can be estimated by observations on the hyperfine splitting. The method however is not very accurate.
The Zeeman effect of the microwave spectra has also been studied by some workers from which the magnetic moments of several nuclei (e.g., $^{33}$S, $^{129}$I) have been determined.

Finally the mass difference between two isotopes of an element can be determined very accurately by measuring the frequency shift of the absorption lines in the hyperfine structure of the microwave spectra, as one isotope is substituted by another in a molecule (see discussion on isotope effect in § 8.11).

8.18 Determination of the electric quadrupole moments of nuclei

Nuclear electric quadrupole moments can be estimated from observations on the departures from the interval rule mentioned in § 8.10, according to which the energy difference between two states $F$ and $F - 1$ for given $J$ (electronic angular momentum quantum number) and $I$ is linearly proportional to $F$ where $F = J + I$. The departures can occur due to two reasons: (a) magnetic perturbations of the nearby levels and (b) effect of the nuclear electric quadrupole moment.

In the second case, the interaction of the nuclear electric quadrupole moment with the electric field of the electrons gives rise to the appearance of additional hyperfine structure lines, which do not obey the interval rule due to magnetic interaction between $I$ and $J$. The existence of the electric quadrupole moment of the deuteron was discovered by this method. It has the value $Q_d = 2.82 \times 10^{-31}$ m$^2$.

As mentioned in § 8.17, the electric quadrupole moment of the nucleus can also be estimated from the hyperfine structure of the microwave spectra of the molecules containing the nuclei in several cases.

The electrostatic interaction energy between the nucleus of an atom in the molecule and the remaining charges (electronic and nuclear) depends on the electric quadrupole coupling coefficient given by

$$q = e Q \frac{\partial^2 V^e}{\partial z^2} \bigg|_0$$

where $V^e$ is the potential due to all charges external to the nucleus under consideration.

The second derivative is determined at the position of the nucleus along the symmetry axis of the molecule.

We can obtain an estimate of the interaction energy of a nuclear electric quadrupole in the electric field due to all the charges external to the nucleus from the following classical considerations. Assuming the field $E$ to be cylindrically symmetric with the symmetry axis along $z$ and taking into account the variation of the field over the nuclear volume we can write

$$E_z = (E_z)_0 + \left( \frac{\partial E_z}{\partial z} \right)_0 = K z$$

where we have assumed the field at the nucleus to be zero and have put

$$K = \left( \frac{\partial E_z}{\partial z} \right)_0$$

Since the source producing the field $E$ is away from the nucleus, $\nabla \cdot E = 0$. This is possible if we write

$$E_x = -K x/2 \text{ and } E_y = -K y/2$$

for a cylindrically symmetric field.

In Appendix AI, it is shown that the interaction energy of an electric quadrupole in an external electric field is given by

$$U_z = -\frac{1}{6} \sum_i \sum_j Q_{ij} \left( \frac{\partial E_x}{\partial x} \right)_0$$

where $i, j$ can take up the values 1, 2, 3 each corresponding to the three rectangular coordinates $x = x_1$, $y = x_2$, $z = x_3$. The quadrupole moment tensor $Q_{ij}$ is given by

$$Q_{ij} = \int \rho(r) (3x_i x_j - r^2 \delta_{ij}) d^3 r$$

where $\rho(r)$ is the density of the charge distribution. Since $Q_{ij}$ is a symmetric tensor, only the diagonal components $Q_{xx} = Q_{11}$, $Q_{yy} = Q_{22}$ and $Q_{xx} = Q_{33}$ are nonvanishing. Also the sum of the diagonal elements is zero:

$$Q_{11} + Q_{22} + Q_{33} = 0$$

So, for an axially symmetric charge distribution (as for an ellipsoid of revolution)

$$Q_{11} = Q_{22} = Q_{33} = -Q \text{ (say)}$$

where $Q = Q_{33}$ is called the quadrupole moment of the charge distribution. We then have ($\because Q_{ij} = 0$ for $i \neq j$)

$$U_z = -\frac{1}{6} \left( Q_{xx} \left( \frac{\partial E_x}{\partial x} \right)_0 + Q_{yy} \left( \frac{\partial E_y}{\partial y} \right)_0 + Q_{zz} \left( \frac{\partial E_z}{\partial z} \right)_0 \right)
- \frac{1}{6} \left( Q_{11} \frac{K}{2} + Q_{22} \frac{K}{2} + Q \frac{K}{2} \right)
- \frac{1}{4} \left( Q \frac{\partial^2 V^e}{\partial z^2} \right)_0 \bigg|_0$$

It should be noted that since $Q$ is measured in the unit of an area (m$^2$) in nuclear physics, the above expression should be multiplied by the unit of charge e.

The quadrupole coupling coefficient $q$ can be determined from observations on the hyperfine splitting in the microwave spectra. However, for the determination of the nuclear electric quadrupole moment $Q$ from the values of $q$, one must know the value of $\left( \frac{\partial^2 V^e}{\partial z^2} \right)_0$. Various methods have been developed for estimating this quantity. However, there
are uncertainties in such estimates which introduce considerable error in the determination of \( Q \).

Linear triatomic molecules, such as CICN, BrCN, OCS etc. and symmetric top molecules like CH\(_3\)Cl and CH\(_3\)Br have been studied by this method.

References


Problems

1. An ion of mass \( M \) carrying charge \( q \) is accelerated through a potential difference \( V \) and then subjected to a uniform magnetic induction field \( B \). If \( R \) is the radius of curvature of the ion path, then prove that

\[
MR^2 = \frac{VqB^2}{2qB^2} = 4.818 \times 10^7 \text{ B}^2 \text{R}^2
\]

Here \( M \) is expressed in u and \( q \) is one electronic unit of charge.

2. Argon ions (singly charged) suitably accelerated are mass-analyzed by a Bainbridge mass spectograph. The electric and magnetic fields in the velocity filter are 1.5 \( \times 10^4 \) volts per metre and 0.4 T respectively. If the ions then enter the magnetic field of 0.9 T what will be the distances between the ion focus lines on the photographic plate for the three isotopes 36Ar, 38Ar and 40Ar? What is the velocity of the ions emerging from the velocity filter?

(1.73 mm; 3.75 \( \times 10^4 \) m/s)

3. Calculate the magnetic fields required to focus the \( \text{O}^+ \), \( \text{CO}^+ \) and \( \text{CO}_2^+ \) ions in a Dempster type single focusing mass spectrometer if \( V = 1000 \) volts and \( R = 0.15 \) m.

(0.1214 T; 0.1606 T; 0.20138 T)

4. The mass differences of the following doublets, which have been determined accurately, can be written as

\[
H_2^+ - H^+ = \alpha \quad \text{for } A/n = 2
\]
\[
H^+_3 + ^{12}\text{C}^{2+} = \beta \quad \text{for } A/n = 6
\]
\[
(12\text{C}^+L_4^+ - ^{16}\text{O}^+) = \gamma \quad \text{for } A/n = 16
\]

Express the masses of \( H^+ \), \( H_2^+ \) and \( ^{16}\text{O} \) in terms of the measured quantities \( \alpha \), \( \beta \) and \( \gamma \).

5. Assuming the magnetic moment of \( ^7\text{Li} \) to be 3.242 \( \mu_n \) calculate the force on a \( ^7\text{Li} \) nucleus in an inhomogenous magnetic field of field gradient \( 10^3 \text{T/m} \) if \( M_1 = 3/2 \).

6. What is the energy difference between the successive states of different spin orientations of \( ^7\text{Li} \) (\( I = 3/2 \)) in a homogenous magnetic field of 1 T? Hence calculate the Larmor precessional frequency.

In a molecular beam experiment of Rabi, the central magnet of length 10 cm produces a steady field \( B_0 = 1 \) T. If the source temperature is 100 K and hydrogen atoms are used as the experimental atoms, plot the probability of spin-reversal due to an oscillating field of \( 10^{-4} \) T as a function of the frequency of the field. What is the resonance frequency?

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