Chapter 2
Review of Literature & Lie Algebraic Theory

The concept of groups was actually introduced about 150 years ago. The theory of groups was developed by a group of famous mathematicians Gauss, Cauchy, Abel, Hamilton, Galois, Sylvester, Cayley and many others. However, Lie groups and Lie algebra were introduced by Marius Sophus Lie and it should be noted that Lie algebraic methods have been useful in Physics in the 1930s. The algebraic approach started as the key tool for the construction of spectra originated in elementary particle physics in the 1960s by H. A. Bethe, E. P. Wigner and others and had major applications in the nuclear physics at the end of the 19th century, especially after the development of Quantum Mechanics in the first part of the 20th century. At present, the group theory has become indispensable in most branches of physics and chemical physics. It may be noted here that although a mathematician is generally more interested in the formal development of abstract group theory, a physicist finds the representation theory of groups of direct use in quantum physics and other branches of physics (Iachello and Oss, 1991; Hamermesh, M., 1962; Gilmore, R., 1974; Wybourne, B. G., 1974; Barut and Raczka, 1986; Miller, W. Jr., 1968; Talman, J. D., 1968; Vilenkin, N. I. 1956, ; Miller, W. Jr., 1977; Olver, P. I., 1986; Joshi, A. W., 2005).

2.1 Concept of a group

Let us consider the set I of all integers, I = { ..., -3, -2, -1, 0, 1, 2, ... }, and also let us consider the following four properties of this set:

(i) The sum of any two elements of the set I is again an integer and hence belongs to the set I.
(ii) The set contains an element 0, called zero, which has the property that for any element \( m \in I \), \( m + 0 = 0 + m = m \).

(iii) For every element \( m \) of \( I \), there exists a unique element \( n \) also belonging to \( I \), such that \( m + n = n + m = 0 \); evidently, \( n = -m \).

(iv) If \( m, n, \) and \( p \) are any three elements of \( I \), \( m + (n + p) = (m + n) + p \); this means that the law of addition is associative.

Let us consider another set, the set \( U(n) \) of all unitary matrices of order \( n \), where \( n \) is a fixed finite positive integer. This set has the following four properties:

(i) If \( U \) and \( V \) are any two unitary matrices of order \( n \), their product \( UV \) is again a unitary matrix of order \( n \) and hence belongs to the set \( U(n) \).

(ii) The set contains the unit matrix \( I \) which has the property \( UI = IU = U \) for every \( U \in U(n) \).

(iii) If \( U \) is an element of \( U(n) \), there exists a unique element \( V \) also in \( U(n) \) such that \( UV = VU = I \).

(iv) If \( U, V \) and \( W \) are any three elements of the set, \( U(VW) = (UV)W \).

It may be noticed that the four properties satisfied by the above two sets are very much similar in nature. These properties, in fact, define a group and both the sets discussed above are the examples of a group. In connection with a group further we may note the following terms.
The number of elements in a group is called its order. When a group contains a finite number of elements, it is called a finite group. If a group contains an infinite number of elements, it is called an infinite group. Further, an infinite group may be either discrete or continuous. In case the number of the elements in a group is denumerably infinite (such as the number of all integers), the group is discrete. On the other hand, if the number of the elements in a group is non-denumerably infinite (such as the number of all real numbers), the group is continuous.

2.2 Lie groups

A group in which the law of composition and the law of inversion are continuous in all the group elements, is called a topological group. The dependence of the elements \( x_1, x_2, \text{ etc.} \), of a topological group \( G \) on its \( r \) continuous parameters can be written explicitly as \( x_1 = x_1(a_1, a_2, \ldots, a_r), \quad x_2 = x_2(b_1, b_2, \ldots, b_r), \text{ etc.} \) Let \( x_1x_2 = x_3(c_1, c_2, \ldots, c_r) \) and \( x_1^{-1} = x_4(d_1, d_2, \ldots, d_r) \). The parameters of \( x_3 \) and \( x_4 \) can be expressed as functions of the parameters of \( x_1 \) and \( x_2 \), that is,

\[
\begin{align*}
c_i &= c_i(a_1, a_2, \ldots, a_r; b_1, b_2, \ldots, b_r), \\
d_i &= d_i(a_1, a_2, \ldots, a_r),
\end{align*}
\] (2.1)

for \( 1 \leq i \leq r \). A topological group is called an \( r \)-dimensional Lie group if there exists a neighborhood \( N \) of the identity element \( e \) such that the continuous parameters of the product of two elements and those of the inverse of an element in \( N \) are continuous differentiable functions of the parameters of the elements, that is, if \( c_s \) and \( d_s \) of (2.1) are analytic functions of \( a_s \) and \( b_s \) for elements in \( N \) provided that \( x_3 \) and \( x_4 \) lie in \( N \) when \( x_1 \) and \( x_2 \) do. In addition, there will be laws for combining the other \( n-r \) discrete parameters.
We see that it is convenient to choose the continuous parameters of a Lie group such that the image of the identity element e is the origin of the parameter space, i.e., \( e = x(0, 0, 0, \ldots, 0) \). Having this parameterization, due to the analytical properties of the Lie groups, an element near the identity may be written as

\[
x(0,0,\ldots,e_j,\ldots,0) = x(0,0,\ldots,0) + i\varepsilon_j I_j(0,0,\ldots,0),
\]

(2.2)

to first order in \( \varepsilon_j \). The operator \( I_j \) can be obtained from (2.2) and is given by

\[
I_j = \lim_{\varepsilon_j \to 0} \left[ (1/i\varepsilon_j) \{ x(0,\ldots,e_j,\ldots,0) - x(0,0,\ldots,0) \} \right]
\]

(2.3)

For a Lie group, all the properties can be derived from the \( r \) operators \( I_j \) (\( 1 \leq j \leq r \)) which need to be defined only near the identity element of the group.

We can arrive at an element of the group at a finite distance apart from the identity by the successive application of the product rule. Thus, let us say that we wish to generate the element \( x(0,0,\ldots,a_j,\ldots,0) \). To do the same, let us first write \( a_j = N \varepsilon_j \), where \( N \) is a large positive integer so that \( \varepsilon_j \) is a small quantity. Then

\[
x(0,0,\ldots,a_j,\ldots,0) = x(0,0,\ldots,e_j,\ldots,0)^N
= [e + i\varepsilon_j I_j]^N
= [e + i(a_j/N)I_j]^N
\]

(2.4)

Now, allowing \( N \) to tend to infinity and using the algebraic identity

\[
\lim_{N \to \infty} (1 + x/N)^N = \exp(x),
\]

we have from Equation(2.4)
\[ x ( 0, 0, \ldots, a_j, \ldots, 0 ) = \exp(i a_j I_j) \] (2.5)

which is an exact result. We are to understand the exponential function on the right-hand side of Equation (2.5) as being formally equivalent to its expansion in the powers of the operator \( I_j \). It may be noted that for a general element of the group, we can easily extend the above result to obtain

\[ x(a_1, a_2, \ldots, a_r) = \exp \left( \sum_{j=1}^{r} i a_j I_j \right) \] (2.6)

Here we note that all the elements of the Lie group belonging to the subset containing the identity can be obtained by giving various values to the parameters \( a_j \) on the respective prescribed intervals. That is why the operators \( I_j \) are called the generators of the Lie group. Also we should note here that with \( r \) continuous parameters a Lie group has \( r \) generators.

### 2.3 Lie algebras and representations of Lie groups

Let us consider a Lie group with \( r \) continuous parameters \( a_k \) having the \( r \) generators \( I_1, I_2, \ldots, I_r \). It is seen that any element of the Lie group can be expressed in the form

\[ x(a_1, a_2, \ldots, a_r) = \exp \left( i \sum_{k=1}^{r} a_k I_k \right) \] (2.7)

For a finite group, It is seen that all the properties of the group can be obtained from the structure of its multiplication table. Here, one may have query regarding what is the equivalent of the multiplication table for a continuous group? It can be shown that for a Lie group, the commutators of its generators determine the structure of the group.

[34]
Thus, let us consider two particular elements of the Lie group of the form

\[ x(0,0,\ldots,a_k,\ldots,0) = \exp(i a_k l_k), \]

\[ x(0,0,\ldots,a_l,\ldots,0) = \exp(i a_l l_l). \]

Here, the product of these two elements, \( \exp(i a_k l_k) \exp(i a_l l_l) \), must belong to the group and hence must be expressible in the form (1.28) with some values of the parameters \( a_k \). Since the generators of a Lie group do not, in general commute with each other (they commute only when the Lie group under consideration is abelian), there is no simple way of writing this product element. However, we may use the fact that such a product involves the commutator of \( l_k \) and \( l_l \). Now, for the product \( \exp(i a_k l_k) \exp(i a_l l_l) \) to belong to the group, it therefore follows that the commutator \([ l_k, l_l ]\) must be a linear combination of the generators, i.e.,

\[
[l_k, l_l] = \sum_{j=1}^{r} c_{klj} l_j, \quad 1 \leq k, l \leq r
\]  \hspace{1cm} (2.8)

where \( c_{klj} \) are certain coefficients. It is known that the commutators of pairs of generators of a Lie group determine the structure of the Lie group completely in analogy with the multiplication table for a finite group. Hence the coefficients \( c_{klj} \) are known as the structure constants of the Lie group. These structure constants are the characteristic property of the Lie group and do not depend on any particular representation of the generators. Since the generators of a Lie group themselves are not unique, hence these structure constants are also not unique.

It is known to us that any linear combination of the generators with real coefficients can also be used as a generator of the group. Hence we can say that the \( r \) generators of a Lie group are the bases for an \( r \)-dimensional real linear vector space.

[35]
Equation (2.8) provides us with a law of composition between any two elements of the vector space such that the resulting vector is also an element of the vector space. In fact, the set of real linear combinations of the generators of a Lie group is a Lie algebra.

A Lie algebra is a real $r$-dimensional vector space $L$ with elements $(x, y, z, \ldots)$ endowed with a law of composition for any two elements of $L$ denoted by $[x, y]$ such that

(i) $[x, y] \in L,$

(ii) $[x, y] = -[y, x], \quad (2.9)$

(iii) $[x, [y, z]] + [y, [z, x]] + [z, [x, y]] = 0$

For all $x, y, z \in L.$ We refer the law of composition $[x, y]$ as the commutator of $x$ and $y.$ In analogy with the basis for a vector space, a set of $r$ independent vectors of $L$ is called a basis of the Lie algebra.

The commutators of the generators of a Lie group defined in equation (2.8) satisfy the above properties, hence we obtain the following relations among the structure constants:

$$C^j_{kl} = -C^j_{lk},$$

$$\sum_{m=1}^{r} \left[ C^{m}_{kl} C^{j}_{jm} + C^{m}_{lj} C^{j}_{km} + C^{m}_{jk} C^{j}_{lm} \right] = 0$$

Since the generators $I_k$ are Hermitian, equation (2.8) shows that the structure constants $c^j_{kl}$ are purely imaginary.

It may be noted here that the importance of the Lie algebra lies in the fact that we may generate a representation of the Lie group by considering a
matrix representation of the Lie algebra. Now, if we are able to find a set of \( r \) square matrices all of order \( p \) (let us say), such that they satisfy the commutation relations (2.8) with the given structure constants, then using these for the \( l_k \)s in equation (2.7), we would generate a \( p \)-dimensional representation of the Lie group. Thus, we can take it as a general rule that a representation of a Lie algebra can be used to generate a representation of the associated Lie group.

Let us now apply the above discussion to SU(2), as an example. The three generators of SU(2) can be chosen to be the Pauli spin matrices

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},
\]

(2.10)

which are a set of three independent traceless Hermitian matrices of order 2. For the generators of U(2) we can then choose the set \( (E, \sigma_x, \sigma_y, \sigma_z) \), where \( E \) is the unit matrix of order 2.

The generators of SU(2) given in (1.30) satisfy the commutation relations

\[
[\sigma_j, \sigma_k] = 2i \sum_l \epsilon_{jkl} \sigma_l,
\]

(2.11)

here \( \epsilon_{jkl} \) is the fully antisymmetric tensor of rank 3 whose only nonvanishing elements are

\[
\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = -\epsilon_{213} = -\epsilon_{132} = -\epsilon_{321} = 1
\]

(2.12)

Here the indices \( j, k, l \) stand for any of \( x, y, z \) or for \( 1, 2, 3 \). It should be noted here that the six equations in (1.33) is generally abbreviated into a single equation and is written as ‘\( \epsilon_{123} = 1 \) and all permutations with proper signs’. One
can see here that the components of the tensor $\varepsilon_{ijkl}$ multiplied by $2i$ are evidently the structure constants of SU(2). Thus, the Lie algebra of SU(2) is the set of all real linear combinations of $\sigma_x$, $\sigma_y$, and $\sigma_z$.

To make the conception more clear let us now look at the following three matrices:

$$
\lambda_1 = \begin{bmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}, \quad \lambda_2 = \begin{bmatrix}
0 & -i & 0 \\
i & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}, \quad \lambda_3 = \begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 0
\end{bmatrix}
$$

(2.13)

We can easily verify that all these three matrices satisfy the same commutation relations as the generators $\sigma$s, i.e.,

$$
[\lambda_j, \lambda_k] = 2i \sum_j \varepsilon_{jkl} \lambda_l.
$$

(2.14)

Thus we see that the $\lambda$s generate a representation of the Lie algebra of SU(2) and can therefore be used to generate a three-dimensional representation of SU(2) itself.

For a Lie group, the maximum number of mutually commuting generators is called its rank. Thus, the rank of SO(3) is 1 because no two of its generators $L_x$, $L_y$ and $L_z$ commute with each other. On the same reasoning, the rank of SU(2) is also 1.

Casimir operator for a Lie group is the operator which commutes with all the generators of the Lie group. The number of independent Casimir operators of a Lie group is equal to its rank. Casimir himself recognized that one such operator could always be constructed by taking a suitable bilinear combination of the generators.

Thus, the one and only Casimir operator of SO(3) is $L^2 = L_x^2 + L_y^2 + L_z^2$, which commutes with each of $L_x$, $L_y$ and $L_z$. Similarly, the only Casimir operator of SU(2) is $\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2$.

[38]
The Casimir operators of a Lie group can be diagonalized simultaneously with its generators. Hence the eigenvalues of the Casimir operators may be used to label the IR of the Lie group. The Casimir operator $L^2$ of SO(3) thus has the eigenvalues $l(l+1)$, where $l$ takes on all nonnegative integral values, and hence the IR of SO(3) may be labeled by the index $l$. The Casimir operator $\sigma^2$ of SU(2) has, in general, the eigenvalues $j(j+1)$ where $j$ takes all nonnegative integral and half-odd-integral values [the representation (2.11) for the generators is a special case with $j=1/2$]. Hence, the IR of SU(2) can be labeled by $j$.

On the basis of the brief discussion on Lie groups and Lie algebras made in this section now we are in a position to summarize the properties of the Lie algebras which are given in the following section.

### 2.4 Properties of Lie algebras

The properties of Lie algebra which are extensively used in this work can be explained on the basis of the following points.

**A. Definition**

Let us consider a set of operators as $X_a$ $(a = 1, \ldots, r)$. If this set of operators satisfying the commutation relations

$$[X_a, X_b] = \sum_c c_{ab}^c X_c,$$

(2.15)

with

$$c_{ab}^c = -c_{ba}^c, \quad [X_a, X_a] = 0,$$

(2.16)

and the Jacobi identity

$$[ [X_a, X_b], X_c ] + [ [X_b, X_c], X_a ] + [ [X_c, X_a], X_b ] = 0,$$

(2.17)
it is said to form a Lie algebra $G$

$$X_a \in G.$$  \hspace{1cm} \text{(2.18)}

In a similar way, a subalgebra $G'$ of $G$ also can be defined. Let us consider a subset $Y_i$ of the $X_a$s. Now if

$$[Y_i, Y_j] = \sum_k c_{ij}^k Y_k,$$  \hspace{1cm} \text{(2.19)}

the subset $Y_i$ of the $X_a$s is said to form a subalgebra $G'$ of $G$. We denote this situation by

$$X_a \in G, \quad Y_i \in G', \quad G \in G'.$$  \hspace{1cm} \text{(2.20)}

We say an algebra (or subalgebra) as Abelian if all its elements commute

$$[X_a, X_b] = 0,$$  \hspace{1cm} \text{for any } X_a \in G.  \hspace{1cm} \text{(2.21)}

\section*{B. Generators and realizations}

It is important to note that for the purpose of the definition of an algebra it is not necessary to specify any explicit form of the operators. If one writes the operators as differential operators, they are said to be the generators of the corresponding group of transformations. In such a case the resulting algebraic structure is said to be a realization (of the abstract algebra). We can also realize the abstract algebraic structure with a set of matrices or with products of creation and annihilation operators.

\section*{C. Cartan classification}

Here we give the Cartan's classification of all the admissible, semisimple, Lie algebras in table 2.1 (Iachello and Levine, 1996; S. Oss, 1996; Frank and Isacker, 1994).
### Table 2.1 Admissible Lie algebras

<table>
<thead>
<tr>
<th>Name</th>
<th>Label</th>
<th>Cartan label</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Special] Unitary</td>
<td><a href="n">SU</a></td>
<td>A_{n-1}</td>
</tr>
<tr>
<td>[Special] Orthogonal</td>
<td><a href="n">SO</a>, n=odd</td>
<td>B_{(n-1)/2}</td>
</tr>
<tr>
<td>[Special] Orthogonal</td>
<td><a href="n">SO</a>, n=even</td>
<td>D_{n/2}</td>
</tr>
<tr>
<td>Symplectic</td>
<td>Sp(n), n=even</td>
<td>C_{n/2}</td>
</tr>
<tr>
<td>Exceptional</td>
<td>G_2, F_4, E_6, F_7, E_8</td>
<td>G_2, F_4, E_6, F_7, E_8</td>
</tr>
</tbody>
</table>

Algebras should be denoted by lower case letters, and their associated groups of transformations by capital letters. We thus see that SO(3) denotes the algebra of special orthogonal transformations in three (3) dimensions, while SO(3) denotes the associated group. However, it has become customary, to denote both groups and algebras by capital letters.

We note that the letter $S$ denotes special transformations, that is, transformations with determinant $+1$. Also it should be noted that when dealing with algebras, the letter $S$ is not important for orthogonal algebras, $B$ and $D$ types, while it is important for unitary algebras, since U(n) and SU(n) differ in the number of operators. One can see here that both orthogonal and special orthogonal algebras have the same number of operators. When dealing with orthogonal algebras, the letter $S$ is deleted in the text to avoid unnecessary burdening of the notation.

### D. Number of operators in the algebra

We know the number of operators in the algebra, denoted by $r$ in section 2.4 A, for any admissible Lie algebra. We call this number as the order of the algebra and is given in table 2.2.
Table 2.2  Number of the operators in Lie algebras

<table>
<thead>
<tr>
<th>Algebra</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(n)</td>
<td>$n^2$</td>
</tr>
<tr>
<td>SU(n)</td>
<td>$n^2 - 1$</td>
</tr>
<tr>
<td>SO(n)</td>
<td>$\frac{1}{2}[n(n - 1)]$</td>
</tr>
<tr>
<td>Sp(n)</td>
<td>$\frac{1}{2}[n(n + 1)]$</td>
</tr>
<tr>
<td>$G_2$</td>
<td>14</td>
</tr>
<tr>
<td>$F_4$</td>
<td>52</td>
</tr>
<tr>
<td>$E_6$</td>
<td>78</td>
</tr>
<tr>
<td>$E_7$</td>
<td>133</td>
</tr>
<tr>
<td>$E_8$</td>
<td>248</td>
</tr>
</tbody>
</table>

E. Isomorphic Lie algebras

It is noted that some algebras have identical commutation relations. Hence we call them as isomorphic algebras. Here we show a list of isomorphic algebras (of low order) in table 2.3. The sign $\oplus$ in table 2.3 denotes direct sums of the algebra, i.e., addition of the corresponding operators. It should be noted here that there is also the trivial case, $U(1) \approx SO(2)$.

Table 2.3  Isomorphic Lie algebras

<table>
<thead>
<tr>
<th>Cartan notation</th>
<th>Isomorphic algebras</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1 \cong B_1 \cong C_1$</td>
<td>$SU(2) \cong SO(3) \cong Sp(2)$</td>
</tr>
<tr>
<td>$B_2 \cong C_2$</td>
<td>$SO(5) \cong Sp(4)$</td>
</tr>
<tr>
<td>$D_2 \cong A_1 \oplus A_1$</td>
<td>$SO(4) \cong SU(2) \oplus SU(2) \cong SO(3) \oplus SO(3)$$\cong Sp(2) \oplus Sp(2)$</td>
</tr>
<tr>
<td>$A_3 \cong D_3$</td>
<td>$SU(4) \cong SO(6)$</td>
</tr>
</tbody>
</table>
F. Casimir operators

We can construct a set of operators for any Lie algebra, called invariant or Casimir operators, $C$, such that

$$[ C , X_i ] = 0 \quad \text{for any} \quad X_i \in G_i$$  (2.22)

i.e., the operators $C$ commute with all the elements of the algebra (Quak M., 1990; Bitto and Huber, 1992). Hence they are called as invariant operators. It may be noted that the operators $C$ can be linear, quadratic, cubic, ....... in the $X$s.

$$C_p = \sum f_{a_1 a_2 \ldots a_p} X_{a_1} X_{a_2} \ldots X_{a_p}. \quad (2.23)$$

A Casimir operator is called of order $p$ when it is containing $p$ operators $X$. It is seen that only unitary algebras $U(n)$ have linear Casimir operators and all other algebras have Casimir operators that are quadratic, cubic, ....... Also we note that if $C$ commutes with all the $X$'s, so does the product of $C$ by any constant ($\alpha C$) and any power of $C$. However, these do not count as new operators. It may be noted here that the number of independent Casimir operators of a Lie algebra is termed as the rank of the algebra.

G. Example of Lie algebras

It is known that the simplest example of a Lie algebra is the angular momentum algebra. One can see that this algebra is a realization of $SO(3)$ and has three elements, the three components of the angular momentum

$$G = J_x, \ J_y, \ J_z,$$  (2.24)
with commutation relations

\[ [J_x, J_y] = iJ_z, \quad [J_y, J_x] = iJ_z, \quad [J_z, J_x] = iJ_y. \quad (2.25) \]

We see that SO(3) has a (trivial) subalgebra, SO(2), composed of only one component, \( J_z \) (let us say),

\[ G' = J_z, \quad (2.26) \]

satisfying the (trivial) commutation relation

\[ [J_z, J_x] = 0 \quad (2.27) \]

One should note here that the algebra of SO(3) has only one independent Casimir invariant

\[ C(\text{SO}(3)) = J_x^2 + J_y^2 + J_z^2 = J^2 \quad (2.28) \]

Hence it is an algebra of rank 1. Cartan called this algebra as \( B_1 \).

It may be noted that the subalgebra SO(2) also has a (trivial) Casimir invariant, i.e., \( J_z \) itself,

\[ C(\text{SO}(2)) = J_z^2. \quad (2.29) \]

Which is also a trivial algebra of rank 1. This algebra was called as \( D_1 \) by Cartan. It may be noted that the invariant operators are important because they are related to conserved quantities. As an example, here we may refer the case of angular momentum.
H. Representations

When we apply Lie algebras in the solutions of problems in physics and chemistry, we need to construct representations of the algebras. It is known that these are linear vector spaces over which the group elements act. We note that the representations of Lie algebras are characterized by a set of numbers (quantum numbers) that can take either integer or half-integer values. Those which take integer values are called tensor representations, while those that take half-integer values are called spinor representations. Another important point here we are to note is the concept of irreducible representations, i.e., vector spaces that transform into themselves by the operations of the algebra, and cannot be further reduced.

We note that the irreducible representations of unitary algebras, U(n), are characterized by a set of n integers, corresponding to all possible partitions of an integer s,

\[ \lambda_1 + \lambda_2 + \ldots + \lambda_n = s, \quad \text{with} \quad \lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_n. \]  

(2.29)

We often arrange the integers \( \lambda \)s into a diagram, called a Young diagram (or tableau). In the Young diagram, the first row is \( \lambda_1 \), the second is \( \lambda_2 \), and so on.

\[
\begin{array}{c}
\lambda_1 \\
OOOOO \\
\lambda_2 \\
OOO \\
\lambda_3 \\
OO \\
\end{array}
\]  

(2.30)

Also we can use another notation which is \([ \lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n \]). In this notation, for example, the diagram (2.30) may be stated as (Iachello and Arima, 1974; Arima and Iachello, 1975; Quak. M., 1990).
It may be noted that the irreducible representations of special unitary algebras, SU(n), are characterized by a set of integers, as in the case of U(n), but with one fewer, i.e.,

\[ \lambda_1 + \lambda_2 + \ldots + \lambda_{n-1} = s, \text{ with } \lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_{n-1} \]  

(2.31)

Also we note that the irreducible representations of SO(n) are characterized by a set of integers, but corresponding to the partition

\[ \mu_1 + \mu_2 + \mu_3 + \ldots + \mu_\nu = s, \text{ with } \mu_1 \geq \mu_2 \geq \ldots \geq \mu_\nu. \]  

(2.32)

where

\[ \nu = \begin{cases} \frac{n}{2}, & n \text{ even}, \\ n - \frac{1}{2}, & n \text{ odd}. \end{cases} \]  

(2.33)

Similarly, the irreducible representations of Sp(n) are also characterized by a set of integers

\[ \mu_1 + \mu_2 + \mu_3 + \ldots + \mu_\nu = s, \text{ with } \mu_1 \geq \mu_2 \geq \ldots \geq \mu_\nu, \]

where, \[ \nu = \frac{n}{2}. \]  

(2.34)

The summary of the discussion made in section 2.4 H is shown in table 2.4, where the results for the exceptional algebras are also given. It may be noted that the number of integers that characterize the representations is also equal to the rank of the algebra.
Table 2.4  Number of integers that characterize the tensor representations of Lie algebras

<table>
<thead>
<tr>
<th>Algebra</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(n)</td>
<td>n</td>
</tr>
<tr>
<td>SU(n)</td>
<td>n - 1</td>
</tr>
<tr>
<td>SO(n), n=even</td>
<td>n/2</td>
</tr>
<tr>
<td>SO(n), n=odd</td>
<td>(n - 1)/2</td>
</tr>
<tr>
<td>Sp(n)</td>
<td>n/2</td>
</tr>
<tr>
<td>G_2</td>
<td>2</td>
</tr>
<tr>
<td>F_4</td>
<td>4</td>
</tr>
<tr>
<td>E_6</td>
<td>6</td>
</tr>
<tr>
<td>E_7</td>
<td>7</td>
</tr>
<tr>
<td>E_8</td>
<td>8</td>
</tr>
</tbody>
</table>

Also it may be noted that there is a complication that arises only when dealing with orthogonal algebras in an even number of dimensions, SO(n), n = even. We see, the complication is that the partition (equation 2.32) is not sufficient to characterize uniquely the representations since there are, two equivalent representations (Hamermesh, M., 1962), when the last quantum number, $\mu_v$, is different from zero. We denote this either by writing explicitly

$$[ \mu_1, \mu_2, \mu_3, \ldots, \pm \mu_v ], \quad \mu_v > 0,$$

(2.35)

or by writing simply

$$[ \mu_1, \mu_2, \mu_3, \ldots, |\mu_4| ],$$

(2.36)

and remembering that there are two such states. In molecular physics SO(4) and SO(2) play an important role. Hence the complication (representation 2.35) cannot be overlooked. Here one should note that the complication (representation 2.35) has also an explicit physical meaning, since it is associated, for example, with the
double degeneracy of $\pi$, $\delta$, .............. orbitals or the $\Pi$, $\Delta$, ....... vibrational states in linear molecules.

I. Tensor products

We can form tensor products with the representations of Section 2.4. H. Generally we denote Tensor products by the symbol $\otimes$,

\[
[ \lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n ] \otimes [ \lambda'_1, \lambda'_2, \lambda'_3, \ldots, \lambda'_n ]
\]  

(2.37)

It may be noted that there are definite rules on how to multiply representations of which we state here one (Hamermesh, M., 1962). Let us consider the product of any representation, for example,

\[
(2.38)
\]

by a one-row representation, for example,

\[
(2.39)
\]

Let us draw the pattern for the first factor, using a symbol, for example, $a$,

\[
\begin{array}{c}
a  \\
a \\
\end{array}
\]

(2.40)

Let us assign another symbol, for example, $b$, to the second pattern. Let us apply $b$ to $a$ in all possible ways subject to the rule that no two $b$'s appear in the same column.

[48]
\[
\begin{align*}
& a \quad a \quad b \quad b \quad \oplus \quad a \quad a \quad b \quad \oplus \quad a \quad b \quad \oplus \quad a \quad a \\
& a \quad a \quad b \quad a \quad b \quad b \\
& b \quad \quad a
\end{align*}
\]

Example:

\[
[1] \otimes [1] = [2] \otimes [1, 1]
\] (2.41)

J. Branching rules

It is seen that for any given quantum mechanical problem one needs to find the complete set of quantum numbers that characterize uniquely the states of the system. It is clear that this corresponds to finding a complete chain of subalgebras

\[
G \supset G' \supset G'' \supset \ldots
\] (2.42)

For solving this problem, there is a definite mathematical procedure (called the branching problem). When we apply the procedure, we need also to deal with the following question. For the subalgebra \(G'\), what are the representations contained in a given algebra \(G\) (branching rules). It may be noted that this problem is also completely solved, and there exist tables of branching rules.

K. Example of representations of Lie algebras

Once again here we return to the simple example of the angular momentum algebra, \(SO(3)\). The tensor representations of the algebra are characterized by one integer (table 2.5), i.e., the angular momentum quantum number \(J\). In a similar way the representations of \(SO(2)\) are characterized by one
integer (table 2.5), i.e., $M$ the projection of the angular momentum on the $z$ axis. Thus the complete chain of algebras is

$$G \supset G' = \text{SO}(3) \supset \text{SO}(2), \quad (2.43)$$

and the complete set of quantum numbers is

$$\begin{array}{c}
\text{SO}(3) \supset \text{SO}(2) \\
\downarrow \quad \downarrow \\
J \quad M
\end{array} \quad (2.44)$$

Bracket notation of Dirac is used here following standard practice. Corresponding to (representation 2.44), the ket $|J, M\rangle$ is also called a basis state.

It may be noted that according to the branching rules for $\text{SO}(3) \supset \text{SO}(2)$, in the representation $J$ of $\text{SO}(3)$, the values of $M$ are all the integers between $-J$ and $+J$. Again it should be noted that the complication mentioned at the end of the Section 2.4 H, is due to the fact that $\text{SO}(2)$ is in an even number of dimensions.

**L. Eigenvalues of Casimir operators**

In the application of algebraic methods to problems in physics and chemistry another ingredient we need is the eigenvalues of Casimir operators in the representations of Section 2.4 H. We give the known solutions in Table 2.5.

**M. Examples of eigenvalues of Casimir operators**

In table 2.5 we give the eigenvalues of the Casimir operator of $\text{SO}(3)$ in the representation $J$ as

$$<C(\text{SO}(3))> = J \,(J + 1). \quad (2.45)$$
This is a well known result. In a similar way, we can obtain the eigenvalues of the Casimir operator of order 2 of SO(4) in the representation $\tau_1, \tau_2$ as

$$< C(SO(4)) > = \tau_1 (\tau_1 + 2) + \tau_2^2. \quad (2.46)$$

Here we notice that once more a complication arises when dealing with orthogonal algebras in an even number of dimensions, since often these algebras have two Casimir operators of order two. The two operators, in such a case, are distinguished by placing a bar over the second operator. We give the eigenvalues of this operator as

$$< \overline{C}(SO(4)) >= \tau_2 (\tau_1 + 1). \quad (2.47)$$

<table>
<thead>
<tr>
<th>Algebra</th>
<th>Labels</th>
<th>Order</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(n)</td>
<td>$[ f_1, f_2, f_3, \ldots f_n ]$</td>
<td>1</td>
<td>$\sum_{i=1}^{n} f_i = f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\sum_{i=1}^{n} f_i (f_i + n + 1 - 2i)$</td>
</tr>
<tr>
<td>SU(n)</td>
<td>$[ f_1, f_2, \ldots f_n = 0 ]$</td>
<td>2</td>
<td>$\sum_{i=1}^{n} [(f_i - f/n)(f_i + 2n - 2i - f/n)]$</td>
</tr>
<tr>
<td>SO(2n+1)</td>
<td>$[ f_1, f_2, f_3, \ldots f_n ]$</td>
<td>2</td>
<td>$\sum_{i=1}^{n} f_i (f_i + 2n + 1 - 2i)$</td>
</tr>
<tr>
<td>SO(2n)</td>
<td>$[ f_1, f_2, f_3, \ldots f_n ]$</td>
<td>2</td>
<td>$\sum_{i=1}^{n} f_i (f_i + 2n - 2i)$</td>
</tr>
<tr>
<td>Sp(2n)</td>
<td>$[ f_1, f_2, f_3, \ldots f_n ]$</td>
<td>2</td>
<td>$\sum_{i=1}^{n} f_i (f_i + 2n + 2 - 2i)$</td>
</tr>
</tbody>
</table>

[51]
2.5 Molecular Spectroscopy and Theoretical Models

To have proper adjustment with the vast production of experimental observations, theoretical physics is constantly being tested to provide a collection of satisfactory models that can account for the observed spectra of various molecules. In this regard we must remember that molecular spectroscopy is undergoing a radical change not simply as a result of technical advancements. Also we are to remember that as a consequence of new (quite often unexpected) experimental results, an unprecedented effort toward constructing alternative theoretical models and formulating novel ideas has taken place in recent years. For instance, the time-dependent analysis of molecular dynamics may be regarded here as a particular striking example. At present this approach is being applied in both long and short time ranges, by virtue of a corresponding interest in high-resolution stationary-state spectroscopy and in low-resolution spectroscopy, including the resonant anharmonic couplings. Molecular beam techniques, colour center lasers, and pump/probe methods now allow for a better arrangement of situations involving not only the spectroscopic characterization of fundamental modes, but also highly excited levels, intramolecular vibrational energy redistribution (I V R) processes, and atomic clusters. This experimental interest, along with a more-or-less preserving concern for traditional aspects of molecular spectroscopy, is the starting point for understanding the actual panorama of theoretical approaches in this field of activity.

For most aspects of molecular spectroscopy (Heisenberg, W., 1925; Bitto and Huber, 1992), a comprehensive theoretical treatment necessarily has to rely on a Hamiltonian formulation. The typical theoretical procedure used to study a given molecule consists of (i) separation of the electronic and nuclear motions (assuming the Born-Oppenheimer approximation) and (ii) solution of the Schrödinger equation in the potential surface for the rovibrating nuclei. In case the molecule is larger than a diatomic, the potential energy surface is a very complex function, composed of a discouragingly large number of coordinates. To have a
solution of this problem, a standard approach involves approximation of the potential energy surface by convenient analytical functions. The force field method is the widely used procedure of this type, in which one considers small displacements of coordinates from their equilibrium values and thus obtaining a harmonic limit for the potential surface. However, this type of approach, encounters difficulties as soon as one considers highly excited levels, and once more, a large number of parameters are needed to achieve a meaningful result. In the computation of molecular spectra the need for practical methods is, in part, satisfied by introducing semi empirical expansion in powers and products of rotational and vibrational quantum numbers. The Dunham series here provides the preeminent expansion. For this approach, the most serious drawbacks are that (i) no Hamiltonian operator is available (not directly, at least), and (ii) for large polyatomic molecules, one needs a correspondingly large number of parameters. In turn, also these parameters have to be adjusted by a fitting procedure over a conveniently large experimental database, which is not always available.

It is clear from the above discussion that in context to the numerous theoretical and experimental advances made in molecular spectroscopy, the above mentioned theoretical models, are not sufficient to face the situation in its befitting manner. As a result, even though certain answers could be attained, till today many fundamental questions of molecular spectroscopy remain unanswered by extending the above mentioned theoretical models.

2.6 Inception of Lie algebraic methods in modern physics

In the development of science, symmetry may be regarded as an extremely important concept (Iachello and Levine, 1996; S. Oss, 1996; Frank and Isacker, 1994; Iachello and Oss, 2002; Dunham, J. L., 1932; Arima and Iachello, 1975; Iachello and Arima, 1987; Cooper and Levine, 1991). From the both purely theoretical and computational viewpoints, the use of symmetry in physics and other related areas is widely recognized. It may be mentioned here that the word symmetry does not
necessarily have a geometric meaning when applied in modern physics. Also it should be noted here that symmetries beyond geometric ones appeared and started to demonstrate their usefulness after the introduction of quantum mechanics in the first part of the 20th Century. Beauty of symmetry is its connection to a possible invariance in a physical system. Such invariance of a physical system leads directly to conserved quantities, which allow one to observe specific degeneracies in the energy spectrum and to introduce a meaningful labeling scheme for the corresponding eigenstates in a quantum mechanical framework.

To deal with the symmetry arguments, group theory is regarded as the most suitable tool. The continuous Lie groups and algebras are powerful mathematical techniques, particularly for addressing quantum mechanical problems embedded in a group theoretical framework. The matrix or algebraic formulation of quantum mechanics is already successful to show its greater suitability compared with the differential or wave formulation, at least in regard to matters inherent in symmetry problems. The use of Lie algebras in a systematic fashion was first introduced in the 1930's. Weyl, Wigner, Racah and others are the pioneer workers in this field. In particular, point and translation group theory played a fundamental role in solid-state physics, while continuous groups, especially unitary groups, were shown to be invaluable in studies related to nuclear and particle physics.

Interacting boson model, the highest expression of group theoretical methods in nuclear physics was introduced for even-even nuclei in 1975 (Iachello and Arima, 1987) and later the same was extended to more complex nuclear systems. Interacting boson model is important for its unprecedented power in describing virtually any kind of experimental situation in nuclear physics. We should note that the interacting boson model is the first example of a comprehensive theoretical model based on a dynamical symmetry environment. Details of dynamical symmetries in connection with molecular spectroscopy are discussed by many authors (Iachello and Levine, 1996; S. Oss, 1996; Frank and Isacker, 1994; Cooper and Levine, 1991). A Hamiltonian is said to have a dynamical symmetry when its eigenvalues are an analytical function of the quantum numbers.
An example of the latter is the finite Dunham-like expansion of the vibrational term values up to second order in the vibrational quantum numbers, as given in reference (Dunham, J. L., 1932). The important point in a dynamical symmetry is that such an expansion can be derived from a Hamiltonian. For example, such a symmetry for triatomic molecules can be derived on the basis of an U(4)⊗U(4) Lie group. We must be clear about the point that a dynamical symmetry is but an approximation. Even we care to make it mainly for two primary reasons, one related with dynamics and the other with spectroscopy. The time-domain reason is the remarkable accuracy of the results provided by dynamical symmetry. For many molecules, the temporal evolution as predicted by dynamical symmetry is accurate for tens or even hundreds of vibrational periods. As the total energy increases, this will become less the case. Even so, it appears remarkable that in the range of the highest overtones currently accessible to direct excitation, the time evolution is regular for such a long time. It is known that there is no contradiction between the utility of dynamical symmetry in the time domain and its limited accuracy in the frequency domain. The same is best understood in terms of the time dependent approach to spectroscopy. This implies that the spectrum is generated via the time propagation of the nonstationary wave packet created at time zero. Highly resolved spectral details reflect long propagation times. The range of this “long” is determined by the magnitude of $h = 5.31 \text{ ps cm}^{-1}$ or, in reduced units, by the typical stretch or bend frequencies which frequently exceed $10^3 \text{ cm}^{-1}$. Hence an rms accuracy of 10 cm$^{-1}$, not very satisfactory in the frequency domain, is sufficient to follow the molecule over many vibrational periods. An interesting implication of the validity of the dynamical symmetry over many vibrational periods is the separation of time scales in the exploration of phase space. The second motivation for considering dynamical symmetry is that it provides a zero order or “deperturbed” set of states. We then can introduce perturbations, and one advantage of the algebraic approach is that this can be done in a systematic fashion. These perturbations can be related to “resonance coupling” of anharmonic, uncoupled oscillators via a semi-classical analysis. This provides a
connection to the application of nonlinear mechanics to spectroscopy. Algebraic effort is utilized to ensure that zero order dynamical symmetry corresponds to anharmonic oscillators. For this reason, we see that in algebraic method an SU(2) group is used for each one-dimensional oscillator and an SU(4) group is used for each three-dimensional oscillator. We can describe a pair of coupled harmonic oscillator with a single SU(2) group. No doubt that this leads to a simpler zero order basis but the characteristic effects of nonlinear mechanics then arise only from the perturbations. A familiar example of a resonance coupling is the Fermi resonance. In reference it has been shown regarding how to include this coupling by breaking the dynamical symmetry. As a result of the coupling, only the quantum number \(2v_1 + v_2 + 2v_3\) is conserved, while the individual stretch \(v_1\), \(v_3\) and bend \(v_2\) quantum numbers are not. It should be noted that for non bending \(v_2 = 0\) molecules, this coupling is the familiar Darling-Dennison 2:2 resonance between the two stretch modes. Other types of resonances (2:3 resonance) also can be described in an algebraic approach. It may be noted here that dynamical symmetries constitute a big step forward over a conventional use of symmetry arguments, especially those concerning the description and classification of energy spectra denoting specific degeneracy patterns. For a simple understanding one may think that the amount of information gained in going from a degeneracy symmetry to a dynamical one is similar to that obtained in going from a static to a dynamical study of forces acting in a conventional mechanical system. We should note here that dynamical symmetries contain within themselves both the degeneracy aspects of a physical system and the complete machinery for describing transitions among different states (that is, the dynamical behaviour of the physical object at issue). In the extremely compact and convenient framework of Lie groups and algebras all these tasks can be carried out well. The use of group theoretical tools very often allows us to address situations inaccessible by means of conventional methods of quantum mechanics.
It may be noted here that the interacting boson model is a beautiful example of the algebraic, second-quantized formulation of quantum mechanics from the aforementioned viewpoint. Such specialization involves recognizing, within the commutation relations of the creation and annihilation operators, certain Lie algebraic structures and to limit the choice of such operators within specific (invariant) bilinear forms. The existing mathematical apparatus concerning Lie algebras, tensor calculus, and related topics (such as the Wigner-Eckart theorem) is typically applied, in the case of nuclear physics and the interacting boson model, to the building block of the problem at issue, namely an object with five internal degrees of freedom (i.e. an electric quadrupole). Observable quantities like excitation spectra and transition probabilities are then obtained in terms of boson operators, whose transformation properties are closely connected with specific abstract symmetries. This type of boson operators are the algebraic version of both the monopole and quadrupole pairing character of the strong interaction between identical nuclear particles.

Very soon, the above mentioned strategy was applied in the world of molecules. First of all, in the last part of the 20th century, the algebraic models were introduced as a computational tool for the analysis and interpretation of experimental rovibrational spectral of small and medium-sized molecules (Satyanarayana, D. N., 2000; Iachello and Levine, 1996; S. Oss, 1996; Frank and Isacker, 1994; Iachello and Oss, 2002; Banwell, C. N. 1992; Arima and Iachello, 1975; Quak, M., 1990; Sako et al., 1999, 2000). The algebraic models are based on the idea of dynamic symmetry, which, in turn, is expressed through the language of unitary Lie algebras. With the application of these algebraic techniques, one obtains an effective Hamiltonian operator that conveniently describes the rovibrational degrees of freedom of the physical system. In this framework, any specific mechanism relevant for the correct characterization of the molecular dynamics and spectroscopy can be accounted. The important point to be noted here is that the algebraic models contain the same physical information for both ab initio theories (based on the solution of the Schrödinger equation) and semiempirical approaches
(making use of phenomenological expansions in powers of appropriate quantum numbers). Compared with that of interacting boson model, it may be seen that the only difference between nuclei and molecules from the viewpoint of the building blocks used is that when dealing with molecules, one has to start with a diatomic unit. This is equivalent to that of considering boson operators related to the dipole character of the diatom. Consequently, a different dynamical symmetry (of smaller dimension than that of used in nuclear physics) is adopted in the description of molecular systems. It may be noted here that based on its firm footing, the algebraic techniques, at present can demonstrate their suitability to address successfully even quite difficult situations of molecular spectroscopy. It is also already confirmed that the algebraic techniques offer a concrete and complementary technique to conventional approaches.

2.7 The Lie algebraic methods

In order to have a review of the Lie algebraic methods (Halonen and Child, 1982; Satyanarayana, D. N., 2000; Iachello and Levine, 1996; S. Oss, 1996; Frank and Isacker, 1994; Barrow. G. M., 1962; King. G. W., 1964; Hollenberg. J. L., 1970) within the context of molecular spectroscopy, we start with the following brief description of it.

The Lie algebraic methods have been useful in the study of problems in physics, especially after the development of quantum mechanics in the first part of the 20th century. The reason is, quantum mechanics makes use of commutators $[x, p_x] = \hbar$ which are the defining ingredients of Lie algebras. And hence often it is termed that the essence of the algebraic methods can be traced to the Heisenberg’s formulation of quantum mechanics (Herzberg. G., 1945).

Let us consider a quantum mechanical problem in one-dimension with the Hamiltonian

[58]
\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \]  (2.48)

Instead of solving the differential equation \( \Pi \psi(x) = E \psi(x) \) directly, let us consider the case of a harmonic oscillator potential

\[ V(x) = \frac{kx^2}{2} \]  (2.49)

and introduce creation and annihilation operators

\[ a^\dagger = \frac{1}{\sqrt{2}} \left( x - \frac{d}{dx} \right), \]

\[ a = \frac{1}{\sqrt{2}} \left( x + \frac{d}{dx} \right) \]  (2.50)

along with a vacuum state \( |0\rangle \). The Hamiltonian for the harmonic oscillator now may be written as

\[ H = \hbar \omega \left( a^\dagger a + \frac{1}{2} \right) \]  (2.51)

with eigenvalues

\[ E(n) = \hbar \omega \left( n + \frac{1}{2} \right), \quad n = 0, 1, \ldots, \infty \]  (2.52)

and eigenstates

\[ |n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle. \]  (2.53)

The harmonic frequency \( \omega \) is given by

\[ \omega = (k/m)^{1/2}. \]  (2.54)
For a generic potential, let us now expand $V(x)$ in powers of $x$

$$V(x) = \sum_{i=2}^{\infty} k_i x_i$$  \hspace{1cm} (2.55)

that is, in powers of $a^\dagger$, $a$, $a^\dagger a$ and diagonalize it in the space $n = 0, 1, 2, \ldots, N$.

The algebra formed with the set of four operators $a^\dagger$, $a$, $a^\dagger a$, $1$ is called the Heisenberg-Weyl algebra $H(2)$ (the identity $1$ commutes with all operators) and has its commutation relations as

$$[a, a^\dagger] = 1; \quad [a, a^\dagger a] = a; \quad [a^\dagger, a^\dagger a] = a^\dagger$$ \hspace{1cm} (2.56)

The method where the Hamiltonian operator is expanded in powers of operators of $H(2)$ is called algebraic harmonic analysis (Miller and Bondybey, 1983). All manipulations are done here algebraically rather than using differential operators. This is the most important advantage of the method. The matrix elements of the operators, $a^\dagger$, $a$ are the key ingredients here in the algebraic manipulations. The matrix elements of the operators, $a^\dagger$, $a$ (called step up and step down operators) are given by

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle; \quad a |n\rangle = \sqrt{n} |n-1\rangle$$ \hspace{1cm} (2.57)

This is all we need to calculate any observable within the framework of harmonic analysis. It is known to us that molecular potentials often deviate considerably from a harmonic potential. As a result, the expansion of $V(x)$ contains many parameters and the basis in which the diagonalization is done needs to be taken very large i.e. $N \rightarrow \infty$.

We can overcome this difficulty by considering other solvable potential functions which contain anharmonicity from the beginning. A function of this type is the Morse function

[60]
\[ V(x) = V_0 \left[ 1 - \exp \left\{ -a \left( x - x_0 \right) \right\} \right]^2 \]  \hspace{1cm} (2.58)

With the help of a series of transformations, the Schrödinger equation with a Morse potential (Fig 2.1) can be written in terms of an algebra composed of four operators \( F_+, F_-, F_z, N \) satisfying commutation relations

\[ [F_+, F_-] = 2F_z \hspace{0.5cm} [F_x, F_z] = \pm F_z \]  \hspace{1cm} (2.59)

(The operator \( N \) commutes with all elements).

The four operators, as cited above, form a Lie algebra, called \( U(2) \), while the three operators \( F_+, F_-, F_z \) form a Lie algebra, called \( SU(2) \), isomorphic to the angular momentum algebra and hence called quasi-spin algebra.

![Graph](image)

**Fig. 2.1** The Morse potential and its approximation with a harmonic oscillator potential.

When written in terms of these operators, the Hamiltonian for the Morse oscillator takes the simple form

\[ H = E_0 + AF_z^2 \]  \hspace{1cm} (2.60)

[61]
Let us now introduce the vibrational quantum number \( \nu \) related to the eigenvalue \( M \) of \( F_z \) by \( \nu = (N - M)/2 \). The eigenvalues of \( H \), in this situation, can be written as

\[
E(\nu) = E_0 + AN^2 - 4A(N\nu - \nu^2),
\]

\( \nu = 0, 1, \ldots, N/2 \) or \( (N - 1)/2 \) (\( N \) even or odd) \hspace{1cm} (2.61)

also the eigenfunctions can be written as \( |N, \nu\rangle \).

Now we are in a position to write the expression for the energy levels in the familiar form

\[
E(\nu) = \hbar \omega_x (\nu + \frac{1}{2}) - \hbar \omega_x x_c (\nu + \frac{1}{2})^2
\]

(2.62)

This represents an anharmonic oscillator with quadratic anharmonicities. The algebra \( U(2) \) now provides a framework for performing algebraic anharmonic analysis. A generic potential can be expanded in terms of quasi-spin operators \( F_+, F_- \), \( F_z \). All we need are the matrix elements of the step up and step down operators of \( SU(2) \) given by

\[
F_+ |N, \nu\rangle = \sqrt{\nu(N - \nu + 1)} |N, \nu - 1\rangle;
\]

\[
F_- |N, \nu\rangle = \sqrt{(N - \nu)(\nu + 1)} |N, \nu + 1\rangle
\]

(2.63)

It may be noted here that for molecular potentials which are not very different from Morse potential, the expansion converges very quickly, that is, very few terms are needed to obtain an accurate description. The harmonic limit also can be easily recovered from \( U(2) \) using a mathematical procedure called contraction (\( 1/N \to 0 \)). By renormalizing the operators \( F_+ \) and \( F_- \) with \( N_{1/2} \), their matrix elements go over those of the harmonic oscillator in the limit \( N \to \infty \).
It should be noted here that the Morse function is not the only one that can be used to provide a basis for anharmonic analysis. The Poeschl-Teller function (Figure 2.2) is another function of interest in molecular physics, especially for bending vibrations. The Poeschl-Teller function, associated with the Lie algebra U(2) is given by

\[ V(x) = - \frac{V_o}{\cosh^2 ax} \]  

(2.64)

It may be noted here that the algebraic method can be applied to problems in any number of dimensions, in particular two and three dimensions where harmonic analysis is done in terms of the Weyl-Heisenberg algebras \( H(3) \) and \( H(4) \), and anharmonic analysis in terms of the Lie algebras \( U(3) \) and \( U(4) \).

![Graph of the Poeschl-Teller potential](image)

**Fig. 2.2.** The Poeschl-Teller potential.
2.8 The role of algebraic methods

The Lie algebraic formulation discussed above can be used to study problems of relevance in physics and chemistry (Iachello, F., 1981; Kitagawa and Kyogoku, 1978; Gladkov et al., 1978). Particularly, in case of molecules, the formulation can be used to analyze vibrational and rotational spectra. Electronic spectra also can be attacked with the algebraic model. However, the field in which the algebraic method has had most impact is that of vibrational spectroscopy. To deal with the vibrational spectroscopy, following are the important advantages of the algebraic method:

(a) In the energy spectra, from the very beginning anharmonicities are put in.

(b) In the interactions between different modes, anharmonicities are introduced automatically since they are already contained in the matrix elements of the step operators.

(c) The Lie algebraic methods allow us to calculate wave functions and thus observables other than energies, such as intensities of transitions (infrared, Raman, Franck-Condon).

In vibrational spectroscopy, anharmonicities play a very important role. This is the reason why the algebraic methods have found their most useful application here.

2.9 Vibrational spectroscopy and the Lie algebraic method

To discuss the vibrational spectroscopy within the context of the Lie algebraic methods (Satyanarayana, D. N., 2000; Iachello and Arima, 1974; Arima and Iachello, 1975), it is convenient to divide molecules according to their size. We denote molecules with $N = 2$ – 4 atoms as ‘small molecules’, molecules with
N = 5 – 100 atoms as ‘medium-size molecules’, and molecules with N > 100 atoms as ‘macromolecules’.

2.9.1 Small molecules

The coordinate system chosen is an important aspect in the study of molecules. In the study of small molecules, the best set for vibrational analysis is provided by the internal coordinates. For a molecule, if N is the number of atoms, the number of internal coordinates is 3N – 6. In case the molecule is linear, there are 3N – 5 internal coordinates. The Lie algebraic method as applied to the vibrational spectroscopy of small molecules consists in quantizing each internal degree of freedom with the algebra of U(2). For a set of n coupled one-dimensional degrees of freedom, the Hamiltonian is then written in terms of the quasi-spin operators \( F_{+,i} \), \( F_{-,i} \), \( F_{z,i} \) for each degree of freedom i. Here a Hamiltonian often used is

\[
H = E_0 + \sum_{i=1}^{n} A_i F_{z,i}^2 + \sum_{i<j}^{n} B'_{ij} F_{+,i} F_{-,j} + \sum_{i<j}^{n} B_{ij} \left( F_{+,i} F_{-,j} + F_{-,j} F_{+,i} \right) \tag{2.65}
\]

In this Hamiltonian, the first term represents a set of n uncoupled anharmonic oscillators and the additional terms represent coupling between the modes. One can see here that apart from some over all constant, this Hamiltonian is the anharmonic version of the coupled harmonic oscillator Hamiltonian

\[
H = E_0 + \sum_{i=1}^{n} a_i^\dagger a_i + \sum_{i<j}^{n} B'_{ij} (a_i^\dagger a_j^\dagger a_i a_j) + \sum_{i<j}^{n} B_{ij} (a_i^\dagger a_j^\dagger + a_i a_j) \tag{2.66}
\]

It may be noted here that any one of the above Hamiltonians (2.65 or 2.66) can be obtained from the other simply by a simple substitution.
For the linear molecules showing bending vibrations, the motion occurs in a plane perpendicular to the axis of the molecule, that is in two dimensions (Figure 2.3). Therefore these vibrations are quantized with the algebra of U(3). This algebra, i.e. U(3) is composed of nine operators. In case of linear molecules, we thus have one U(2) for each stretching vibration and one U(3) for each bending vibration. The Hamiltonian operator is expanded here in terms of the four operators of U(2) and the nine operators of U(3).

![Diagram of bending vibrations in linear polyatomic molecules.](image)

**Fig. 2.3.** Bending vibrations in linear polyatomic molecules.

Recently this scheme has been used to study the bent and linear molecules. For bent triatomic molecules (SO₂, S₂O) there are three one-dimensional degrees of freedom, quantized with U(2) × U(2) × U(2). In case of linear triatomic molecules (CO₂) there are two one-dimensional stretching modes and one two-dimensional bending mode, U(2) × U(2) × U(3). In a similar fashion, we have for linear four-atomic molecules (C₂H₂), U(2) × U(2) × U(2) × U(3) × U(3). It has been possible to extract the algebraic parameters by fitting the experimental energy levels. In the usual harmonic analysis these parameters play the role of the force-field constants.

For small molecules now let us see the results obtained so far. First of all we consider the usefulness of the Lie algebraic methods and its comparison with
that of usual harmonic analysis. For this, let us consider the Figure 2.4. In this figure the r.m.s. deviation for CO₂ is shown against the number of basis states (Halonen and Child, 1982). The curve 'algebraic' notes the anharmonic analysis and the curve 'conventional' denotes the usual harmonic analysis. From this figure the convergence properties are very much clear. It is known that for CO₂ there are strong Fermi resonances between the double bending vibration and the symmetric stretch. From Figure 2.4 we note that for CO₂ the conventional analysis requires at least 1500 basis states to converge to a good r.m.s. deviation, whereas the algebraic analysis has already converged with less than 1000 states. The another important point of the algebraic method is its ability to calculate vibrational energies to very high quantum numbers. This is feasible here because we start from the beginning with an anharmonic basis. In this basis perturbations and couplings are small. This can be seen in the study of SO₂ where it has been possible to follow the vibrational states up to 20 quanta of vibration. The reliable calculation of highly excited states of molecules makes us capable to answer several important queries. One of the most important queries is on where and how the transition between normal modes and local modes occurs and whether or not chaotic properties emerge at some excitation energy. The analysis of SO₂ and H₂O shows that the transition from normal to local occurs in SO₂ at \( v \approx 18 \), whereas in case of H₂O it occurs already at \( v \approx 2 \) (Halonen and Child, 1982). Most molecules with hydrogen bonds in general show local behaviour for \( v \geq 2 \), although the much more complex dynamics observed in certain molecules (e.g. C₃H₂) are also well described in the algebraic methods (Jacobson et al., 1999; Nesbitt. D. J., 1988; Oss, S. and Temsamani, M.A., 1998; Temsamani et al., 1999).

As already mentioned, one of the main advantages of the algebraic method is that it permits a calculation of transition intensities (infrared, Raman and Franck-Condon). In molecular spectroscopy intensities of transitions have not been much used because of the fact that absolute calibration is often difficult. At present this difficulty has been removed. Recent experimental techniques are there which can extract transition intensities. Definitely, this new advancement will provide an enormous
Fig. 2.4 Convergence properties of the algebraic method as compared with the conventional method (Halonen and Child, 1982)

amount of information on the structure of molecules. To substantiate the comment, the recent study of Franck-Condon intensities in $S_2O$ may be cited as an example[52]. In Lie algebraic method, in the study of transitions, we need a model of the transition operator. We need a dipole moment function in the study of infrared transitions. In case of usual harmonic analysis in one-dimension often this is expanded in powers of the coordinate $x$.

$$M(x) = \sum_{k=0}^{\infty} m_k x^k \quad (2.67)$$

Algebraically we write the equation (2.66) as

$$M = \sum_{k=0}^{\infty} m_k (a + a')^k. \quad (2.68)$$

It may be noted that this dipole moment function also suffers from the same problems of the potential function, that is, here also it becomes difficult to include anharmonicities. The dipole function is expanded in Lie algebraic method in terms of algebraic operators.

[68]
$$M = \sum_{i=0}^{l} m_i (F_e + F_i)^t.$$

(2.69)

In algebraic method the better form often used is

$$M = M_0 \exp[\alpha (F_e + F_i)].$$

(2.70)

The algebraic method provides us a way to perform calculations of transition intensities in which the anharmonicities are included from the beginning both in the potential function and in the transition moment function. Application of this technique has provided an excellent description of 1000 Franck-Condon intensities in S₄O. This technique has made it possible also to extract information on the wave functions of both the upper and lower electronic manifold and information of the extent to which non-Condon effects play a role in these transitions (Saykally, R. J., 1989).

2.9.2 Medium-size molecules

A convenient set of coordinates is provided by the local coordinates for medium size molecules. It may be noted here that this is in contrast to that of small molecules. For local coordinates we have the advantage to write the Hamiltonian operator in a simple form. However, local coordinates have the disadvantage that the spurious coordinates associated with overall transitions and rotations must be removed. We must note that for medium-size molecules, discrete symmetries also play a major role. Due to these two difficulties, medium-size molecules present a real challenge to any calculation. To circumvent these difficulties several techniques have been devised. To circumvent the first difficulty, a technique often used is that of adding to the Hamiltonian a term proportional to the center of mass coordinates and letting the coefficient of that term go to a large value. In case the potential is harmonic, this removal of the center of mass
motion is exact. In other cases it is only approximate and there is a small error in the calculation of the vibrational modes which are admixed with the center of mass motion. In the study of benzene $C_6H_6$, successfully the technique has been used (Hutson J. M., 1990). To circumvent the second difficulty, we can construct symmetry adapted states and operators. Already several methods have been used to sort out this problem. The method introduced by Frank, Lemus and others has been used to formulate algebraic models directly in terms of symmetry adapted operators (Heaven, M. C. et al., 1992). Another method introduced by Chen, has been used to calculate vibrational states with up to $v = 10$ quanta of vibrations in octahedral molecules ($UF_6$) (Wilson et al., 1980). In this area the algebraic methods are found particularly useful since the conventional methods are found difficult to apply here. The algebraic methods made it possible to analyze several phenomena of particular importance in medium-size molecules, the most important one is the question of vibrational energy redistribution.

Recently, using Lie algebraic method (Sarkar et al., 2006, 2008a, 2008b, 2009 Choudhury et al., 2008, 2009; Karumury et al., 2008, 2009a, 2009b, 2009c, 2009d, 2010) reported better results for the vibrational energy levels of some linear triatomic molecules and other tetrahedral & poly atomic molecules than those reported earlier.

2.9.3 Macromolecules

Local coordinates are the best choice for macromolecules. There is no problem in removing the spurious center of mass motion since its role is negligible when the overall mass of the molecule is large. Here the role of discrete symmetries is also less prominent in comparison to that of medium-size molecules. Macromolecules still to be taken within the framework of the algebraic methods. The information on vibrational spectroscopy of these systems is also not fully acquired. Under such circumstances, a joint venture of theoretical and experimental studies is essential to have a deep understanding of the structure of macromolecules.