CHAPTER 2

CONSTRUCTION OF THE TIME EVOLUTION OPERATOR FOR ANHARMONIC SYSTEMS: A LIE - ALGEBRAIC APPROACH.
2.1 INTRODUCTION

Dynamics of nonstationary states on anharmonic potential surfaces plays a major role in several processes of chemical interest. Molecular collision dynamics, unimolecular reactions, photodissociation reactions are some of the examples of phenomena that are controlled by dynamics on such surfaces.

The simplest approach to calculate such dynamics is to expand the time dependent wave function as a linear superposition of the basis vectors of an appropriate Hilbert space. However, the computational effort in such an approach scales exponentially with the number of degrees of freedom in the system, rendering it intractable for systems with more than three to four degrees of freedom at present [1]. This basis set bottleneck has prompted several authors to look for alternative approaches to study anharmonic dynamics [2-15,16].

One such method which received attention in recent years is the Lie-algebraic method [2-8,17,18]. The essential feature of the algebraic approaches is the realization that if the hamiltonian is an element of a Lie-algebra,

\[ H = \sum \hbar_{ij} a^i_a^j, \]  \hspace{1cm} (2.1.1a)

\[ [a^i_a^j, a^k_a^l] = \sum_{ij} \delta_{ik} a^j_a^l - \sum_{ij} \delta_{ij} a^k_a^l, \] \hspace{1cm} (2.1.1b)

the time evolution operator can be parametrized as the exponential of an antihermitean element of that algebra [16,17].

\[ U = \exp(X), \] \hspace{1cm} (2.1.2a)
\[ X = -X^+ = Z \times l \quad i \]  

(2.1.2b)

Here the coefficients \( C \) are called the structure constants of the algebra.

The governing equations for the coefficients of the generators of the evolution operator are obtained by substituting the ansatz (2.1.2a) into the Schrödinger's equation for the evolution operator

\[ i U^1 U = U^1 H U \quad . \]  

(2.1.3)

Expanding both sides of eq.(2.1.3) by the well known Hausdorff expansion and equating the coefficients of each 1 on either side of the equation provides the required working equations. The resulting expressions are compact and provide a convenient route for generating the solution to eq.(2.1.3) either perturbatively as is done in Magnus expansion [16] or non-perturbatively [2-6].

The advantages of the algebraic method are most striking when the Lie-algebra is finite dimensional. In this case, the number of independent variables required to define the evolution operator globally is finite, even if the underlying Hilbert space is infinite dimensional. The most general class of hamiltonians that belong to a finite dimensional Lie-algebra, other than the projection operator algebra operative in finite dimensional vector spaces, are the quadratic hamiltonians. Consequently, a large body of studies have appeared in which quadratic hamiltonians which belong to the harmonic oscillator algebra have been studied by the Lie-algebraic method [2-6] and the
closely related gaussian wave packet propagation techniques [8-12]. Since most problems of practical interest require dynamics on anharmonic surfaces, the harmonic oscillator algebra cannot provide an exact solution for the evolution operator of such systems. Instead, the algebraic theory is used to develop an intermediate picture representation [2] in which the convergence pattern of the time dependent wave function is improved compared to that in the conventional basis set expansion approach. To this end, a model wave function $\psi$ is defined and related to the exact wave function $\psi_0$ by a unitary transformation $U_e$.

$$\psi = U_e \phi.$$  \hspace{1cm} (2.1.4a)

The model wave function then satisfies the equation

$$i \dot{\phi} = (U_e^\dagger H U_e - i U_e^\dagger U_e) \phi.$$  \hspace{1cm} (2.1.4b)

It is now postulated that the $U$ operator is generated by the elements of the harmonic oscillator algebra $L_u$

$$U_e = \exp \left\{ \sum_i l_i \right\} ; \quad l_i \in L_u = \{ q, p, q^2, p^2, qp, pq, 1 \}$$  \hspace{1cm} (2.1.5)

Here $q$ and $p$ are the coordinate and momentum operators. Given that $l$ belong to an algebra, it is possible to define an intermediate reference hamiltonian $H$ by

$$i \dot{U_e} = H U_e.$$  \hspace{1cm} (2.1.6)

where $H$ is also an element of $L$. Consequently, eq(2.1.4b) can
be rewritten as

\[ i \phi = U^{-1} (H - H_e) U \phi. \quad (2.1.7) \]

The model wave function \( \phi \) is now expanded in terms of the basis vectors \( x \) of the Hilbert space,

\[ \phi = \sum_n C_n x_n. \quad (2.1.8) \]

The (possibly time dependent) coefficients appearing in \( H \) (eq.(2.1.6)) are now chosen such that the expansion in eq.(2.1.8) converges rapidly. Several recipes are discussed in literature to attain this goal. In the simplest approach, \([2,5,6,8]\) \( H \) is chosen so as to cancel all linear and bilinear terms in \( H \). It is implicitly assumed in this case that the interaction potential has fast converging Taylor series and that the first two terms are the most important. On the other hand, Shi and Rabitz [4] and Kucar and Meyer [3] have suggested the usage of time dependent variational principles to obtain \( H \). More recently Echave et al [2f] suggested an alternative to the exponential ansatz of eq(2.1.5). These authors observe that the unitary transformation \( U \) acting on the elements of the algebra generates elements of the algebra again. Thus,

\[ U^{-1} \mathbf{1} U = \sum y_{ij} \mathbf{1}_j. \quad (2.1.9) \]

If the hamiltonian is an analytical function of the basis operators of the algebra, this transformation yields

\[ -1 \quad U^{-1} H (1) U = H (U^{-1} \mathbf{1} U). \quad (2.1.10) \]
Instead of the coefficients \( x \) in the exponential ansatz, the mixing coefficients \( y \) are now to be determined so as to optimize the convergence in eq(2.1.10).

A common feature shared by all the above approaches is to use the harmonic oscillator algebra to define an intermediate Hamiltonian which generates the basis functions such that fewest possible basis functions would provide the converged time dependent wave function. In other words, they utilize the harmonic oscillator algebra to construct an explicitly time dependent reference Hamiltonian which generates a convenient time dependent basis set. The dynamical calculations are then carried out by the conventional linear superposition method or the perturbation theory.

In this chapter, we present a completely Lie-algebraic method for the calculation of dynamics generated by anharmonic Hamiltonians that bypasses the basis set expansion. All anharmonic Hamiltonians with fixed number of degrees of freedom are elements of a single infinite dimensional Lie-algebra. Thus they can all be treated on the same generic footing irrespective of the specific interaction potential that characterises the system. These algebras are introduced in Sec. 2.2a along with a discussion on the difficulties encountered when a canonical representation of the evolution operator such as eq.(2.1.2) is invoked. Briefly, these consist of the following: Since the algebra is infinite dimensional, the number of independent variables required to parametrize the evolution operator is also infinity. Consequently, truncations are necessary in any practical calculation. Even then, the governing equations for the generators of the evolution operator contain infinite order
polynomials of the unknown coefficients necessitating further approximations. In addition, under some exotic conditions, the existence of the solution is also questionable.

These problems can be surmounted by parametrizing the evolution operator in a non-canonical product of exponential operators. Wie and Norman [18] and Wolf and Korsche [19] have discussed a reduction principle when the algebra under consideration has an invariant sub-algebra. More recently this reduction principle was extended to algebras which have only non-invariant subalgebras by Sree latha and Prasad [20]. This reduction principle is reviewed in Sec. 2.2b. We then use it to construct the time-evolution operator for a general 1-d anharmonic oscillator in Sect 2.2c.

The algebra of the anharmonic oscillators can be realized either in the coordinate space in the form of differential operators or equivalently, in the boson ladder operator form in the Hilbert space spanned by the harmonic oscillator eigenfunctions. The evolution operator generated by the algebraic approach in the boson operator representation turns out to be the time dependent generalization [21] of the ansatz postulated by the coupled cluster method [22-30] (CCM) for the anharmonic oscillators [31-36]. The concepts invoked in the CCM such as the cluster decomposition property [22] and the subsystem embedding condition [25] emerge naturally in the algebraic approach. It turns out that the usage of the Wie-Norman product form in which the operator sequence is chosen by the reduction principle eliminates both the problems encountered in the construction of the anharmonic evolution operator by the algebraic approach. Generalizations to multidimensional systems are discussed in
Sec. 2.2c. Finally, in the last section, we conclude with a general discussion of the method.

2.2. METHODOLOGY

2.2a. The Algebra of the Anharmonic Oscillators.

We now turn to the construction of the time evolution operator for anharmonic oscillators. For concreteness, we discuss one dimensional systems below. The most general form of the hamiltonian in such a case is

\[ H = \frac{p^2}{2m} + \sum_{n=0}^{\infty} \frac{1}{n!} V_n q^n. \]  

(2.2.1a)

Here \( q \) and \( p \) are the coordinate and the momentum operators of the particle, \( m \) is the mass and \( V \) are the coefficients appearing in the Taylor series for the potential energy function. Note that we make no assumptions regarding the potential energy function other than that it has a well defined Taylor series. This hamiltonian is an element of the infinite dimensional Lie-algebra \( L_0 \)

\[ L = \{ Q_q = q^m p^n ; 0 \leq ra.n \leq \infty \} \]  

(2.2.2a)

(unless the summation in eq.(2.2.1a) is restricted to at most quadratic terms). To see this consider the commutator of the cubic term in the potential with \( p^2 \) operator.

\[ \{ q^3, p^2 \} = 6 \hbar^2 q + 6i\hbar q^2 p. \]  

(2.2.3a)
The commutator of the second term in this operator with $q^3$ once again gives

$$\{q^2p, q^3\} = -3i\hbar q^4,$$  \hspace{1cm} (2.2.3b)

while the commutator of the second term with $p^2$ operator gives

$$\{q^2p, p^2\} = 2\hbar^2p + 4i\hbar qp^2$$  \hspace{1cm} (2.2.3c)

Continuing in this vein, we find that the algebra is not closed until all the operators of the form $q \cdot p$ are included in it. Since this result is independent of the particular set of coefficients appearing in the Taylor series for the interaction potential in eq.(2.2.1a), all one dimensional anharmonic hamiltonians belong to this infinite dimensional Lie-algebra. Transforming to the harmonic oscillator ladder operator representation, we have

$$H = \sum_{m,n} h_{mn} a^+^m a^n.$$  \hspace{1cm} (2.2.1b)

Here $a^+$ and $a$ are the usual harmonic oscillator ladder operators defined as

$$a^+ = \left[ m\omega \cdot q + i \left( \frac{1}{m\omega} \right) p \right] / \sqrt{2} \hbar$$

$$a = \left[ (m\omega) \cdot q - i \left( \frac{1}{m\omega} \right) p \right] / \sqrt{2} \hbar$$
where to is an arbitrary parameter. In this representation, \( L_0 \) is given by

\[
L_0 = \{ A_{mn} = a^{+m} a^n ; \ 0 \leq m, n \leq \infty \}.
\]  

(2.2.2b)

We shall make use of this representation in the following discussion. Given that \( H \) is an element of \( L_0 \), we can parametrize the evolution operator \( U \) as

\[
U \cdot \exp \{ S \},
\]

(2.2.4a)

\[
S = \sum_{m,n=0}^{\infty} S_{mn} a^{+m} a^n ; \quad S_{mn} = - S_{nm}^*.
\]

(2.2.4b)

This representation runs into two difficulties. To begin with, even when the summation for \( S \) operator in eq.(2.2.4) is restricted to some finite values of \( m \) and \( n \) \((m,n \geq 2)\), the Hausdorff expansion gives a non-terminating series. To see this consider a truncation of \( S \) with only two terms in it, \( S_{30} a^{+2} \) and \( S_{-a} a^3 \) and one term in \( H \) containing only \( a \). Then,

\[
U^{-1} H U = \exp[-S_{30} a^{+3} + S_{03} a^3] a \exp[S_{30} a^{+3} - S_{03} a^3]
\]

\[
= a + 3S_{30} a^{+2} + 3S_{30} S_{03}(6a + 6a^+ a^a)/2! +
\]

\[
18S_{30} S_{03} (3S_{30} a^{+2} + 6S_{30} a^{+3}a + 3S_{03} a^4 + 6a^+ a^2)/3! + \ldots
\]

(2.2.5)

Note that at each alternate order a \( a \) term is once again
generated. Thus, even when the operator set in eq.(2.2.4b) is 
**restricted** to a few terms, the coefficients of all operators in 
$U^m H U$ would contain infinite order polynomials in $S$. Since 
little is known about the magnitudes of $S$ *a priori*, it becomes 
difficult to evaluate them numerically without invoking some 
further *approximations*. The second problem with the 
**representation** (2.2.4) is that under some conditions the 
governing equations are not well defined. This can be seen by 
considering

$$U^{-1} \frac{d}{dt} U \sim \exp \left[ -(S_{30}a^3 + S_{03}a^3) \right] \frac{d}{dt} \exp \left[ S_{30}a^3 - S_{03}a^3 \right]$$

$$= \frac{d}{dt} + \dot{S}_{30}a^3 - \dot{S}_{03}a^3$$

$$+ \frac{1}{2!} \left[ \left( 9a^2 + a^2 + 18a + 6 \right) \left( S_{30}S_{03} - S_{30}\dot{S}_{03} \right) \right]$$

$$+ \frac{54}{3!} \left[ \left( S_{30}S_{03} - S_{30}\dot{S}_{03} \right) \left\{ \left( a^4 + a^3 + \ldots \right)S_{30} \right\} \right] + \ldots \ldots$$

$$= \frac{d}{dt} + \frac{54}{3!} \left( S_{30} + 2S_{30}S_{03}S_{30} + 2S_{03}S_{30}S_{03} + \ldots \right) a^3 + \ldots$$

(2.2.6)

As can be seen, the coefficient of the $a$ operator is $S_{30}$ 
multiplied by a polynomial function of $S_{30}$ and $S_{03}$. If this 
function were to become zero at some point of the evolution, then 
$S_{30}$ would not be defined.

Both these problems arise because the ansatz (2.2.4) treats
stepup and stepdown operators on equal footing. As a consequence, the multi commutator expansion becomes a non-terminating series. If these two sets of operators are disentangled and written as separate exponentials these difficulties would not appear. This provides the motivation for invoking a Wei-Norman product form for the evolution operator. In Sec. 2.2b we discuss a reduction principle by which such a disentanglement of operators can be achieved in a systematic fashion by exploiting the sub-algebra structure of L and in Sec.2.2c we will use it to construct the evolution operator for the 1-d enharmonic oscillators. Extensions to multidimensional AHOs will be presented in Sec.2.2d.

2.2b. Reduction principle and decoupling of the algebraic evolution operator.

In this sub-section we present the details of the reduction principle by which the evolution operator can be written as a product of exponentials whose equations of motion are decoupled from each other.

Consider now the situation where the Lie-algebra L containing the hamiltonian \( H \) has a sub-algebra \( L_1 \) spanned by the operator set \( \{ I_i^1 \} \) and define \( C_0 \) as the difference of \( L_0 \) and \( L_1 \)

\[
C_0 = \{ I_i^0 \} = L_0 - L_1 \subseteq L_0. \tag{2.2.7a}
\]

If \( U \) is parametrized as

\[
U = U_0 U_R, \tag{2.2.7b}
\]

\[
U_0 = \exp (X_0), \tag{2.2.7c}
\]

63
\[ x_0 = \sum_i x_i^0 l_i^0 ; l_i^0 = c_0, \]  
(2.2.7(1))

the governing equation for \( U_n \) is obtained by substituting eq. (2.2.7b) in the TDSE and is given by

\[ iU_R = H_R U_R, \]  
(2.2.8a)

\[ H_R = U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0. \]  
(2.2.8b)

Note that by eq. (2.2.8), \( U_n \) is generated by the effective \textit{Hamiltonian} \( H_n \). Thus an exponential \textit{representation} of \( U \) is generated by the operator basis of the algebra to which \( H_n \) belongs. In general, \( H_R \) belongs to \( L_0 \), since by Hausdorff expansion eq. (2.2.8b) gives

\[ H_R = \sum_i \bar{h}_i(x^0) l_i - i \sum_i \dot{x}_i^0 \left\{ f_{ij} (x^0) l_j \right\}, \]  
(2.2.8c)

where \( h \) are functions transformed Hamiltonian matrix elements. These and \( f \) are functions of the structure constants of the algebra. However it is possible to restrict \( H_n \) to \( L_0 \), by requiring that all the coefficients of the \( l_i \) operators in \( H_n \) vanish. With this it would now be possible to parametrize \( U_n \) strictly in terms of the operators of \( L \) alone. Since \( C_0 \) does not contain any of the operators belonging to \( L \), this leads to a product form of \( U \) in which the governing equations for the
coefficients of the operators in \( C_\mathcal{O} \) are decoupled from the coefficients of the operators in \( L \). Since the number of \( x \) variables is equal to the number of operators \( 1 \) in \( C_\mathcal{O} \) by definition (eq.(2.2.7d)), these equations can always be satisfied. Formally this can be written as,

\[
( U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0 ) 1^0 = 0
\]  

(2.2.8d)

which becomes the working equation for \( U_0 \). With eq. (2.2.8d) satisfied and consequently \( H_1 \) restricted to \( L \), \( U_D \) can now be parametrized as

\[
U_R = \exp (X_1)
\]  

(2.2.8e)

\[
X_1 = \sum_i x_1^i 1_{L_1}^i ; \quad 1_{L_1}^i \in L_1.
\]  

(2.2.8f)

Note that to solve eq(2.2.8d) for \( x \) coefficients, no knowledge of the \( x^1 \) coefficients is needed. Thus, the two sets of equations for \( x \) and \( X \) coefficients are decoupled from each other. The result of eq (2.2.7) – (2.2.8) can easily be generalized to a situation when \( L_0 \) has a sequence of sub algebras \( L \) such that \( L \supset L \supset L_2 \ldots \). The evolution operator can be factorized as

\[
U = \prod_k U_k,
\]  

(2.2.9a)

\[
U_k = \exp (X_k)
\]  

(2.2.9b)

\[
X_k = \sum_k x_k^i 1_{L_k}^i ; \quad 1_{L_k}^i \in C_k = L_k - L_{k+1}.
\]  

(2.2.9c)
The decoupled equations of motion for the coefficients of the generators are given by

\[( U_k^{-1} \bar{H}_k U_k - i \dot{U}_k U_k ) \big|_{k=1} = 0, \quad (2.2.10a) \]

\[\bar{H}_k = U_{k-1}^{-1} \bar{H}_{k-1} U_{k-1} - i \dot{U}_{k-1} U_{k-1}. \quad (2.2.10b)\]

As a concrete example, consider the dynamics generated by a quadratic Hamiltonian:

\[H = \omega a^+ a^{} + f(a^+ + a^{}) + g(a^+ a^+ + aa^{}). \quad (2.2.11)\]

This Hamiltonian is an element of the harmonic oscillator algebra \(L_n = \{ a, a^+, a a, a a, a a, a, 1 \}\). This algebra has several sequences of sub-algebras. We discuss one of them here.

\[L_H \supset L_1 \supset \ldots \ldots \quad (2.2.12a)\]

with

\[L_1 = \{ a^+ a, a a, a, 1 \}. \quad (2.2.12b)\]

It can readily be verified that \(L_1\) is closed under commutation. The difference of \(L_0\) and \(L_1\) is given by

\[C_0 = L_H - L_1 = \{ a^+, a^+ a^{} \}. \quad (2.2.12c)\]

Thus in the first step we write \(U\) as the product of two exponential operators \(U\) and \(U\) where \(U\) is generated by the
operators in $C_0$ alone and $U_R$ is generated by the operators in $L$ alone.

\[ U = U_0 U_R \]  \hspace{1cm} (2.2.13a)

\[ U_0 = \exp (S) \]  \hspace{1cm} (2.2.13b)

\[ S = S_{10} a^+ + S_{20} a^+ a^+. \]  \hspace{1cm} (2.2.13c)

According to eq. (2.2.8a), the governing equation for $U_n$ is given by

\[ i \dot{U}_R = H_R U_R \]  \hspace{1cm} (2.2.14a)

where,

\[ H_R = U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0. \]  \hspace{1cm} (2.2.14b)

Evaluating these terms we find

\[ U_0^{-1} H U_0 = \exp (-S) H \exp (S) \]

\[ = H + [H, S] + [[H, S], S]/2! + ... \]

\[ = \omega a^+ a^+ + f(a^+ a^+) + g(a^+ a^+ a^+ a^+) + \omega S_{10} a^+ + 2\omega S_{20} a^+ a^+ \]

\[ + fS_{10} + 2fS_{20} a^+ + 2gS_{10} a^+ + 4gS_{20} a^+ a^+ + 2gS_{20} + \]

\[ + (2gS_{10}^2 + 4gS_{20} S_{10} a^+ + 8gS_{10} S_{20} a^+ a^+) /2! \]  \hspace{1cm} (2.2.15a)

and
To achieve the decoupling of the equations of motion of \( U_+ \) and \( U_- \), we need to set the coefficients of the operators belonging to \( C \) in \( H_R \) as zero (Cf. eq. (2.2.8)). This is achieved by setting

\[
i S_{10} = f + \omega S_{10} + 2f S_{20} + 4g S_{20} S_{10} \tag{2.2.15c}
\]

\[
i S_{20} = g + 2\omega S_{20} + 4g S_{20}^2 \tag{2.2.15d}
\]

With these equations satisfied, \( H_R \) takes the form

\[
H_R = (\omega + 4g S_{20}) a^+ a + (f + 2g S_{10}) a + g aa \\
+ (f S_{10} + 2g S_{20} + g S_{10}^2).
\tag{2.2.15e}
\]

Note that this operator contains the operators belonging to \( L = \{a, a^+ a, a a^+, 1\} \) only. To continue further we note that \( L = \{a, a^+ a, a a^+\} \) is a sub-algebra of \( L_+ \). The difference of \( L_+ \) and \( L_0 \) is the identity operator. Thus, the time dependent \( C \)-function in \( H_R \) can be factorized in \( U_\lambda \) to give

\[
U_R = U_c U_1, \tag{2.2.18a}
\]

\[
U_c = \exp (S_{00}), \tag{2.2.18b}
\]

\[
i S_{00} = f S_{10} + 2g S_{20} + g S_{10}^2. \tag{2.2.18c}
\]
Further, \( L_d = \{ a, aa \} \) is a sub-algebra of \( L_2 \). Thus \( U_1 \) can be parametrized as

\[
U_1 = U_D U_x \quad \text{(2.2.17a)}
\]

\[
U_D = \exp ( S_{11} a^+ a ) \quad \text{(2.2.17b)}
\]

\[
U_x = \exp ( S_{01} a + S_{02} aa ) \quad \text{(2.2.17c)}
\]

The governing equations for these are obtained similarly and give

\[
i S_{11} = \omega + 4g S_{20} \quad \text{(2.2.18a)}
\]

\[
i S_{01} = f + 2g S_{10} \quad \text{(2.2.18b)}
\]

\[
i S_{02} = g \quad \text{(2.2.18c)}
\]

The full evolution operator is thus given by

\[
U = \exp( S_{10} a^+ + S_{20} a^+a^+ ) \exp(S_{00}) \exp(S_{11} a^+a) \exp(S_{01}a + S_{02} aa) \quad \text{(2.2.19)}
\]

Note that the equations of motion for \( S \) and \( S_{20} \) are decoupled from the rest of the coefficient set. Similarly while \( S_{00} \) depends parametrically on \( S_{10} \) and \( S_{20} \), it is decoupled from \( S_{11} \), \( S_{01} \) and \( S \) as was desired. Note that the operator sequence in eq.(2.2.19) is different from that used by earlier authors [2-8]. For example, Benjamin [5] uses the operator ordering
As a consequence, his equations of motion for the coefficients of \( a \) and \( a^a \) depend explicitly on the coefficient of \( a^a \). This is in contrast to our approach where the equation for the coefficients of \( a^a \) and \( a \) are decoupled from the coefficient of \( a^a \).

2.2c. Evolution operator for one dimensional AHO.

We now turn to the construction of the evolution operator of a one dimensional anharmonic oscillator. As mentioned earlier the hamiltonian of such a system, in its most general form, is given in the harmonic oscillator ladder operator representation by

\[
H = \sum_{m,n} h_{mn} a^m a^n. \tag{2.2.20}
\]

There are several ways in which \( L_\alpha \) can be decomposed as envisaged in the previous sub-section. These correspond to different variants of the CCM ansatz \( [29] \). We discuss two versions here. It is convenient for this purpose to classify the operators in \( L_\alpha \) as follows

a. Sets of creation operators

\[
C_k = \{ a^{-(k+n)} a^k ; \ n \geq 1 \} \quad 0 \leq k \leq \omega. \tag{2.2.21a}
\]
b. Sets of annihilation operators

\[ A_k = \{ a^k a^{k+n} ; n \geq 1 \} \quad 0 \leq k \leq \infty. \quad (2.2.21b) \]

c. Sets of diagonal operators

\[ D_k = \{ a^k \} \quad 0 \leq k \leq \infty. \quad (2.2.21c) \]

Consider now the set of operators \( L = L_\mathbb{C} - C_\mathbb{C} \). Other than the identity operator in \( D \), all other operators in this set contain at least one annihilation operator. Consequently, their commutators also contain at least one annihilation operator. To see this we evaluate the commutator of two typical elements of \( L_1 \).

\[
[a^m a^n, a^p a^q] = a^m [a^n a^p a^q] + a^p [a^m a^q] a^n
\]

\[
= \sum_{r=0}^{\text{Min}(n,p)} a^{(m+p-r)} a^{(n+q-r)} n_r p_r - \sum_{r=0}^{\text{Min}(m,q)} a^{(m+p-r)} a^{(n+q-r)} m_r q_r. \quad (2.2.22a)
\]

Since \( n \) and \( q \) are at least 1, and \( r \) is at most either \( q \) or \( n \), the terms with non-zero coefficients contain at least one \( a \) on the right. Thus \( L \) is closed under commutation and hence is a Lie-algebra. Consequently, the time evolution operator can be factorized as
As per the discussion in Sec. 2.2b, the working equations for the coefficient set $S_-$ would be decoupled from the rest of the variables $S_{<n}$ and $r$. Similarly, equation for $S_{00}$ depends upon $S_-$ parametrically, but does not depend upon $r$. Thus at the first stage $U$ is factorized into three terms as follows,

$$ U = U_D U_D' U_R $$

where $U_D$ and $U_R$ are exponential operators generated by the operators in $C$ and $L$ respectively.

$$ U_D = \exp \left( \sum m S_{m0} a^m \right) $$

$$ U_R = \exp \left( \sum m r_m X_m \right) ; \quad X_m \in L_1. $$

Further, the set of operators $L_1' = L_1 - D_0$ is also closed under commutation. Thus, $U_R$ can be further factorized as

$$ U_R = U_{D0} U_R' $$

where $U_{D0}$ and $U_R'$ are exponential operators generated by the operators in $D_0$ and $L_1'$ respectively.

$$ U_{D0} = \exp \left( S_{00} \right) $$

$$ U_R' = \exp \left( \sum m r'_m X'_m \right) ; \quad X'_m \in L_1'. $$

As per the discussion in Sec. 2.2b, the working equations for the coefficient set $S_-$ would be decoupled from the rest of the variables $S_{<n}$ and $r$. Similarly, equation for $S_{00}$ depends upon $S_-$ parametrically, but does not depend upon $r$. Thus at the first stage $U$ is factorized into three terms as follows,

$$ U = U_D U_{D0} U_R $$
Continuing in the same vein, it can be verified that the sets of operators $L_{k+1} = L_k - C_k$ and $L_{k+1} = L_k + D_k$ are sub-algebras of $L_k \supset L_k'$ for all $k$.

The last set in this sequence of sub-algebras is

$$L_\infty = \prod_{k=1}^\infty L_k'$$  \hspace{1cm} (2.2.24a)

This can be further decomposed as follows

$$L_1' = L_\infty - A_0$$  \hspace{1cm} (2.2.24b)

$$L_{k+1}' = L_k' - A_k.$$  \hspace{1cm} (2.2.24c)

Thus the evolution operator after complete factorization reads as

$$U = \prod_{k=0} \left[ \exp \left( W_k \right) \exp \left( Z_k \right) \right] \prod_{l=0} \exp \left( Y_l \right);$$

$$W_k \in C_k, \quad Z_k \in D_k, \quad Y_l \in A_l.$$  \hspace{1cm} (2.2.25a)

$$W_k = \sum_m S_{mk} a^+(m+k)a^k, \quad Y_k = \sum_m y_{mk} a^k a^+(m+k), \quad Z_k = \sum_k S_{kk} a^k a^k.$$  \hspace{1cm} (2.2.25b)

where $m > k \geq 0$.

In the CCM parlance, this ansatz corresponds to the normal coupled cluster method (NCCM) [29].

Returning to the equation of motion for $U_0$
we find

\[ iU^{-1}_0 \dot{U}_0 = i \exp \left( \sum_m - S_{m0} a^{+m} \right) \frac{d}{dt} \exp \left( \sum_m S_{m0} a^{+m} \right) \]

\[ = i \frac{d}{dt} + i \sum S_{m0} a^{+m} \]  \hspace{1cm} (2.2.26b)

since the remaining terms in the Hausdorff expansion are zero. Note that \( S_{m0} \) terms are not multiplied by any function which can go to zero. Hence these equations are free from questions regarding the existence of solutions. Turning now to the second term,

\[ U_0^{-1} H U_0 = H + \sum S_{m0} [H, a^{+m}] + \frac{1}{2!} \sum S_{m0} S_{n0} [H, a^{+m}, a^{+n}] + \ldots \]  \hspace{1cm} (2.2.26c)

we note that the creation operators in \( H \) can be taken out as they commute with \( a \) operators of \( S \). If the hamiltonian term contains \( k \) annihilation operators, the multicommutator expansion terminates after \( k \) nested commutators since no annihilation operators would be left to give a non-zero commutator. Thus the working equations would contain polynomial terms in \( S_{m0} \), no higher than \( k \) power. Suppose now that the truncation index on the cluster operator \( S \) is set equal to \( N \) (i.e., \( \sum_{n=0}^{N} S_{n0} a^{+n} \)). Then the multicommutator expansion gives at most an operator of the form \( +k(N-1) \). Since the approximation requires operators only
upto $a^+ N$, we would need to consider only a subset of these terms. These arguments are easily generalized to show that the rest of the terms in $U$ such as $U_1$, $U_2$, etc., are also free from these two defects unlike the canonical representation eq. (2.1.2).

The advantages of the ansatz (2.2.24) are best demonstrated in the context of the evolution of harmonic oscillator eigenstates. Consider as a first example, the evolution of the vacuum state.

$$U|0\rangle = \exp \left[ \sum_m S_{m0} a^+ a + S_{00} \right] |0\rangle \quad (2.2.27a)$$

since all other generators acting on the vacuum state give zero. Thus, to obtain the dynamics of the vacuum state, only the $S_{m0}$ matrix elements are needed. Similarly, for the first excited state we find,

$$U|1\rangle = \exp \left[ \sum_{m=1} S_{m0} a^+ a + S_{00} \right] \exp \left[ \sum_{m=2} S_{m1} a^+ a \right] \exp\left[ S_{11} a^+ a \right] |1\rangle \quad (2.2.27b)$$

Here the $S_{m0}$ matrix elements remain frozen from the previous calculation for the evaluation of the vacuum state by eq (2.2.26). Thus depending upon the state to be propagated $U$ is automatically restricted.

A second sequence of sub algebras to $L_0$ which yield the evolution operator corresponding to the so called extended coupled cluster method (ECCM) [29] is obtained as follows
The effect of \( U \) on the vacuum state is determined by three sets of parameters since

\[
L_1 = L_0 - C_0
\]
\[
L_1' = L_1 - A_0
\]
\[
L_1'' = L_1 - D_0
\]
\[
L_k = L_{k-1} - C_{k-1}
\]
\[
L_k' = L_k - A_{k-1}
\]
\[
L_k'' = L_k - D_{k-1}
\]

The evolution operator is given by

\[
U = \prod_{k=0}^{\infty} \exp \left( W_k \right) \exp \left( Y_k \right) \exp \left( Z_k \right)
\]

\[
W_k \in C_k, \ Y_k \in A_k, \ Z_k \in D_k.
\]

The effect of \( U \) on the vacuum state is determined by three sets of parameters since

\[
U|0\rangle = \exp \left( \sum_m S_{m0} a^{+m} \right) \exp \left( \sum_m y_{m0} a^m \right) \exp(S_{00}) |0\rangle
\]

The equations of motion for the different cluster amplitudes \( S_\cdot \) are obtained from eq. (2.2.10). When truncations are made in the operator set, these equations also contain finite order polynomials only.

Note that while the coefficients of the annihilation operator have no role to play in the NCCM approach, they influence the diagonal and higher rank cluster operators in the
ECCM. Thus the computational effort in the NCCM is roughly half of that required by ECCM. In general, if one is interested only in the calculation of correlation functions or scattering amplitudes, the NCCM is preferable. On the other hand if expectation values are desired, the ECCM becomes the preferred method. This can be seen from the expressions for expectation values by both approaches over an arbitrary initial state $|m\rangle$.

Since $U^+ = U^{-1}$, we get from eq(2.2.25) for NCCM

$$\langle m | U^+ 0 U | m \rangle_{\text{NCCM}} = \langle m | \prod_{l=m}^{0} \exp (-Y_l) \prod_{k=\infty}^{0} \exp (-Z_k) \exp (-\bar{W}_k) | 0 \rangle$$

$$= \prod_{k=0}^{m} \exp (\bar{W}_k) \exp (Z_k) \prod_{l=0}^{m} \exp (Y_l) | m \rangle.$$  \hspace{1cm} (2.2.32)

The corresponding expression for ECCM is given by

$$\langle m | U^+ 0 U | m \rangle_{\text{ECCM}} = \langle m | \prod_{k=m}^{0} \{ \exp (-Z_k) \exp (-Y_k) \exp (-\bar{W}_k) \} | 0 \rangle \times$$

$$\prod_{k=0}^{m} \{ \exp (\bar{W}_k) \exp (Y_k) \exp (Z_k) \} | m \rangle.$$  \hspace{1cm} (2.2.33)

In the NCCM approach the knowledge of creation operators to all orders is required even if the expectation value is to be evaluated over a few boson states. This is in contrast to the situation in the ECCM where the cluster amplitudes of the creation operators corresponding to the larger boson state are not required.
2.2d. Generalizations to multidimensional systems.

The analysis presented above in the context of a one-dimensional anharmonic oscillator is generalized to multidimensional systems almost trivially. The most general form of the Hamiltonian for a \( D \)-dimensional AHO is given by

\[
H = \sum_{j=1}^{D} \frac{\mathbf{p}_i \mathbf{p}_j}{2m_{ij}} + \sum_{i=1}^{D} V^{(1)}_{1i} q_i + \frac{1}{2!} \sum_{i,j=1}^{D} V^{(2)}_{ij} q_i q_j + \ldots
\]

It can be shown by arguments similar to those for the one-dimensional AHO, that this Hamiltonian is an element of the algebra,

\[
L_0 = \{ \prod_{i=1}^{D} q_i^{n_i} p_i^{m_i} ; 0 \leq n_i, m_i \leq 1 \}
\]

irrespective of the particulars of the interaction potential. We note in passing that the Lie-algebra of 1-d AHOs is a subalgebra of this. In the boson operator representation the Hamiltonian and the algebra take the form

\[
H = \sum_{m_1, n_1 = 0}^{\infty} h(m_1 n_1 m_2 n_2 \ldots \ldots m_D n_D) \prod_{\alpha} a_{\alpha}^{m_\alpha} a_{\alpha}^{n_\alpha}
\]
A sequence of subalgebras similar to the 1-d AHO algebra can be found here also and can be used to factorise the time evolution operator. For example, the multidimensional analogues of $C_0$, $D_0$ and $L_1$ are given by

$$C_0 = \{ \prod a_{\alpha}^{n_{\alpha}} ; \ 0 \leq n_{\alpha} \leq \infty \}. \quad (2.2.36a)$$

$$D_0 = \{ 1 \} \quad (2.2.36b)$$

$$L_1 = \{ \prod a_{\alpha}^{n_{\alpha}} a_{\beta} ; \ 0 \leq n_{\alpha} \leq \infty \}. \quad (2.2.36c)$$

With this, $U$ can be parametrized as

$$U = U_0 \ U_1 \ U_2 \ldots \quad (2.2.37a)$$

$$U_0 = \exp \left[ \sum_{n_1 n_2 \ldots} S^0_{n_1 n_2 \ldots} (a_1^+)^{n_1} (a_2^+)^{n_2} \ldots + S^0_{00} \right]$$

$$U_1 = \exp \left[ \sum_{\alpha \ n_1 n_2 \ldots} S^1_{\alpha n_1 n_2 \ldots} (a_1^+)^{n_1} (a_2^+)^{n_2} \ldots a_\alpha \right]$$

$$\quad \exp \left[ \sum_{\alpha \beta} S^1_{\alpha \beta} a_\alpha^+ a_\beta \right] \quad (2.2.37c)$$

etc. The only complication that arises is that the operators in the diagonal sets lead to non-terminating serieses and unlike in the one dimensional problem where each $D_\alpha$ contains only one
element, these serieses cannot be analytically summed. Since each $D_k$ is a closed algebra, the exponentials involving these operators can be replaced with linear expansions, thus eliminating the infinite serieses. Thus $U$ of eq(2.2.37c) for example, would be given by

$$U_1 = \exp\left[\sum \sum S_{n_1 n_2 \ldots ; \alpha}^{n_1} (a_1^+)^{n_1} (a_2^+)^{n_2} \ldots a_\alpha \right] \left[ \sum \sum U_{\alpha \beta} a_\alpha^+ a_\beta \right].$$

(2.2.37d)

2.3. CONCLUDING REMARKS

Dynamics of initially prepared states on anharmonic surfaces play a fundamental role in many processes of chemical interest. Exponentially repulsive potentials are used to model the dynamics of photodissociation processes and inelastic molecular collisions. Morse functions are used to model highly anharmonic bond stretch motions. Double well functions are used to model potential surfaces on which reactive collisions take place. All these are examples of anharmonic potential energy surfaces [37]. Lie-algebraic approaches to quantum dynamics have attracted considerable attention in recent years primarily because of the advantages such a description has to offer in terms of the compact expressions it provides for the generators of the time evolution operators and the hierarchy of convenient and highly accurate approximation it allows.

In this work, we have constructed the exact time evolution
operator for anharmonic oscillators by the Lie-algebraic method. The hamiltonians of all such systems irrespective of the particular interaction that characterises the system belong to an infinite dimensional algebra. This poses two problems in addition to the number of operators when a canonical representation of a single exponential is used to parameterize the evolution operator. First, the expressions in the equations for the generators contain infinite order polynomials even when the operator set is restricted, necessitating further (and perhaps uncontrolled) approximations. Second, the derivative terms, in the most general case, are multiplied by polynomial functions of the coefficients appearing in the generator of the evolution operator. No unique solution to the corresponding equation is possible if any of these functions were to become zero at some stage of the evolution. We have circumvented these two problems by parameterizing the evolution operator in a Wei-Norman product form. In addition, the equations of motion for different groups of generators were decoupled by invoking a reduction principle.

The algebra of anharmonic oscillators can be realized in two different forms. Adopting the boson ladder operator representation, we found that the resulting algebraic evolution operator is just the time dependent generalization [21] of the CCM wave operator. Realizing that the logarithm of the wave operator is an additively separable operator asymptotically, the CCM postulates an exponential wave operator for the vacuum states

\[ U_c = \exp (S) \quad (2.4.1) \]
and decomposes the cluster operator into one, two, three, ....., N-body excitation operators. Generalizing to the open-shell systems, the CCM posits \[27\]

\[ U = U_C U_V \]  \hspace{1cm} (2.4.2)

where \( U \) is expected to account for core-valence and valence-valence interactions. At this stage, an operator redundancy is found, since the equations corresponding to different operators (for example \( a^+ \) and \( a^{+2} a \)) cannot be separated. To avoid this, the 'subsystem embedding condition' is imposed \[27\]. According to it, the cluster amplitudes corresponding to the fewer particle sub-system remain unchanged when it is embedded in a larger system. Within the framework of the algebraic theory, the subsystem embedding condition emerges naturally, since it is a consequence of the decoupling of the equations of motion of the relevant operators. We have discussed two different orderings of the operators which correspond to the NCCM and ECCM, in this context. Each has its own advantages and depending upon the quantity of computational interest, one or the other becomes the preferred method.

The Lie-algebraic approach offers several formal advantages over the basis set expansion approach. We recall in this context that the formal solutions to the Schroedinger equation is of the exponential form

\[ U = \exp \left( -i\mathcal{H}t \right), \]  \hspace{1cm} (2.4.3)

when the hamiltonian is time independent. Even if the hamiltonian
is explicitly time dependent eq. (2.4.3) holds in the limit of infinitesimal time displacement. Thus, an exponential ansatz for $U$ provides a better formal framework for approximate calculations than an ansatz that depends linearly on its parameters. In addition, the asymptotic separability properties of the time evolution operator are built into it. For example, consider a system which separates into two non-interacting subsystems asymptotically. The hamiltonian of such a system can be written symbolically as

$$\lim_{\epsilon \to 0} H_{\epsilon} = H_A + H_B. \tag{2.4.4}$$

Here, $H_A$ and $H_B$ are the hamiltonians of the two subsystems and $s$ is a measure of the coupling between them. In this limit, the evolution operator factorizes as

$$\lim_{\epsilon \to 0} U = U_A U_B. \tag{2.4.5}$$

Since the sets of operators which act on the Hilbert spaces of the two subsystems commute with each other, and each is closed under commutation separately, they form closed subalgebras of the complete operator set acting on the direct product space of these two Hilbert spaces. Thus, they are decoupled from each other. Parametrizing $U$ in a Wei-Norman product form as suggested in Sec. 2.2b is equivalent to disentangling the excitation and deexcitation operators such that it is in a normally ordered form with respect to the harmonic oscillator basis set.
Lastly, we return to the choice of the basis vectors to the operator space. As mentioned earlier, the AHO operator space can be realized in the coordinate space as $L_0 = \{ q, p ; 0 \leq m, n < \infty \}$ where $q$ and $p$ are the coordinate and momentum operators respectively. The decoupling procedure discussed in Sec.2.2c is operative here also and $L_0$ can be factorised as

a. Sets of coordinate operators

$$C_k = \{ q^{(k+n)} p^k ; n \geq 1 \} \quad 0 \leq k \leq \infty$$

(2.4.6a)

b. Sets of momentum operators

$$A_k = \{ q^k p^{(k+n)} ; n \geq 1 \} \quad 0 \leq k \leq \infty$$

(2.4.6b)

c. Sets of diagonal operators

$$D_k = \{ q^k p^k \} \quad 0 \leq k \leq \infty$$

(2.4.6c)

Continuing further, similar to the decompositions discussed in Sec. 2.2c, the time evolution operator can now be parametrised in two ways:

1) $U = \prod_{k=0}^{\infty} \exp (W_k) \exp (Z_k) \prod_{l=0}^{\infty} \exp (Y_l);$  

$$W_k \in C_k, \quad Z_k \in D_k, \quad Y_l \in A_l \quad (2.2.8)$$

$$W_k = \sum_m s_{mk} q^{(m+k)} p^k, \quad Y_k = \sum_m y_{mk} q^k p^{(m+k)}, \quad Z_k = \sum_k s_{kk} q^k p^k$$

where $m > k \geq 0.$

84
2) \[ U = \prod_{k=0}^{n} \{ \exp (W_k) \exp (Y_k) \exp (Z_k) \}; \]
\[ W_k \in \mathbb{C}^k, Y_k \in \mathbb{A}^k, Z_k \in \mathbb{D}^k. \] (2.2.9)

It is more convenient to keep the momentum operator \( p \) to the right of the coordinate \( q \) as the number of derivatives that result as a consequence of \( p \) would be comparatively less.

An approach based on such a representation would be more convenient if the calculations were being carried out in the coordinate space (such as the grid techniques [1]). The disadvantage of this representation over the boson representation is that there are no natural "annihilation operators" in this case. Thus one is obliged to carry out the calculation by including both \( q \) and \( p \) operators to the same order and accepting non-terminating serieses.

The application of the formalism developed in section 2.2 to a few model systems will be studied in this thesis in the next three chapters. In the third chapter, we will apply the algebraic theory to model one-dimensional systems. In the fourth chapter, application to model two dimensional systems will be presented. Application to the non-adiabatic dynamics for a few realistic systems will be discussed in chapter 5.

We would like to make a note that we will use the words Lie-algebraic method and the time dependent coupled cluster method interchangeably wherever applicable.
REFERENCES