CHAPTER 1

INTRODUCTION
1.1. INTRODUCTION.

Quantum dynamics has developed into an effective tool to study molecular dynamics. Modern technological progress has made it possible to study individual molecular processes with the use of molecular beams and tunable lasers. These experimental studies necessitate the development of new theoretical methods and models to study such processes. This modelling of molecular systems gives a deeper insight into the mechanism of molecular phenomena. Also the simulation of the experimental results is now possible with the advent of high-tech computers.

Studying molecular dynamics using quantum theory essentially involves solving the Schroedinger equation either in the time independent formalism or time dependent formalism [1]. Many problems in molecular dynamics such as spectroscopy, molecular scattering etc. have been traditionally dealt with using the static theory i.e., solving the time independent Schroedinger equation. Later on the time dependent methods have gained a greater importance due to the inherent advantages these methods have to offer. One of the major problems which arises in the application of the static formalism is in the evaluation of spectra. In such an approach all the accessible eigenvalues and eigenstates have to be evaluated to obtain the spectrum irrespective of the resolution required. Such eigenstates can be very large in number even for small molecules and extension to larger molecules becomes very cumbersome and difficult to deal with. In most of the cases the observed experimental spectra do not show all the eigenstates, rather the envelope of spectrum


generated by these states is observed. The time dependent Methods are based on the dynamical evolution of an initially prepared state of the system and do not require evaluating all the eigen states.

Several methods exist in literature to solve the Schroedinger equation in its time dependent formalism. The simplest and accurate method of these is the basis set expansion approach [2]. In this approach, the time dependent wave function is expanded as a linear superposition of the basis vectors of an appropriate Hilbert space.

\[ \psi(t) = \sum_i C_i \phi_i \]  

(1.1.1)

The equations of motion for the coefficients obtained from the time dependent Schroedinger equation (TDSE) are

\[ i\hbar \frac{d}{dt} C_i = \sum_j H_{ij} C_j. \]  

(1.1.2)

Several choices of basis vectors \( \phi \) ranging from discrete variable representations using coordinate space grids to finite basis set representations that use the eigenfunctions of convenient zeroeth order hamiltonian, including mixed mode representations have been discussed in literature along with strategies to implement such calculations [2J. Although the implementation of this method is very simple, the computational effort required to solve for the properties of a system scales exponentially with the number of degrees of freedom in the system. Consequently, dealing with larger systems becomes
impractical. This has prompted several authors to look for alternative approaches. The classical trajectory based methods, the semiclassical methods [2-9] and the pure quantum mechanical methods that use dynamical basis sets are some of them. In the later sections of this chapter, we will discuss the semiclassical GWP (gaussian wave packet propagation), the TDSCF (time dependent self consistent field), the TDCCM (time dependent coupled cluster method) and the Lie-algebraic methods, all of which are related to each other as they involve the usage of the time dependent basis sets.

1.2. GAUSSIAN WAVE PACKET PROPAGATION (GWP) TECHNIQUES.

The semiclassical Gaussian Wave Packet dynamics (GWP) [3] by Heller has received considerable attention in the recent years. The approach parametrises the wave packet as a travelling gaussian

\[ \psi(q,t) = \exp \left\{ \frac{i}{\hbar} \left[ \alpha_t (q - q_t)^2 + p_t (q - q_t) + \gamma_t \right] \right\}, \quad (1.2.1) \]

where \( q_t \) and \( p_t \) are the expectation values of position and momentum respectively, \( \alpha_t \) describes the width of the wave packet during its evolution and \( \gamma_t \) is the phase factor of the wave packet. This approach is exact for harmonic potentials. In the simple gaussian wave packet dynamics the [3-6] potential \( V(q) \) is expanded as a Taylor series around the centroid of the wave packet and truncated at the quadratic level.
This approach works well even for anharmonic systems provided the imaginary part of the width parameter is considerably smaller than the characteristic range over which the potential energy function changes.

Another variant on GWP utilizes the Frenkel - Dirac variational principle [9] to obtain the working equations. Recently, Coalson and Karplus [91 have recast these equations in a convenient form for practical calculations and have applied to the photodissociation dynamics of ICN using the Beswick and Jortner model [10]. Although this procedure does not invoke the locally harmonic approximation and gives a better account of the anharmonicities prevalent in the system, it cannot describe the

\[
V(q) = V(q_t) + (\partial V/\partial q)_{q=q_t} + 1/2! (\partial^2 V/\partial q^2)_{q=q_t} (q - q_t)^2. \tag{1.2.2}
\]

This \textit{approximation} is termed the \textit{local harmonic approximation} (LHA). Substituting eq. (1.2.1) and (1.2.2) in the time dependent Schroedinger equation

\[
\imath \hbar \frac{\partial \psi}{\partial t} = H \psi \tag{1.2.3}
\]

result in the following equations of motion

\[
\begin{align}
q_t &= \frac{p_t}{m}, \tag{1.2.4a} \\
p_t &= - (\partial V/\partial q)_{q=q_t}, \tag{1.2.4b} \\
\alpha_t &= -2 \alpha_t/m - 1/2 (\partial^2 V/\partial q^2)_{q=q_t}, \tag{1.2.4c} \\
\gamma_t &= \imath \hbar \alpha_t/m + P q_t - p_t^2/2m - V_0. \tag{1.2.4d}
\end{align}
\]

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classically forbidden processes such as tunneling and cannot account for the non-gaussian distortions the wave packet eventually undergoes.

The GWP is subject to two limitations. The first is the locally harmonic approximation (LHA). As a consequence of this the wave packet is confined to the classical trajectory. The second which is also a consequence of the LHA is the restriction that the wave packet remains a gaussian throughout the course of its evolution. In the presence of anharmonic perturbations, these restrictions can cause inaccuracies in the final spectrum. For example, in an early study of the Franck-Condon spectrum of a Morse oscillator, Warshel and Hwang [4bl found that the GWP at thawed gaussian approximation did not produce sharp peaks at the quantised energies. More recently Coalson and Karplus [9] observed that the variational GWP in the Hartree approximation gave an artificial negative absorption for a two dimensional dissociative surface. One way of overcoming this drawback is by expanding the initial wave packet as a linear combination of displaced gaussians [5].

\[ \psi = \sum_i c_i g_i \]

The coefficients \( c_i \) can either be kept constant or alternatively can be varied in time. The individual gaussians \( g_i \) are propagated using the GWP prescription. Another way of parametrising the wave packet is by expanding the wave function as

\[ \psi = P(q, q_t)g \]
where \( P \) is a polynomial function of \((q - q)\) \([7,8]\). The parameters in \( g \) are obtained either variationally or non-variational. The approach has been applied to study the photodissociation dynamics of \( \text{CH}_2\) by Lee and Heller \([7]\) and to study atom-diatom scattering by Coalson and Karplus \([8]\). Essentially these methods use GWP to generate a set of time dependent functions which are then used to carry out the dynamical calculations. Inherently it is hoped that since GWP provides fairly accurate description of the dynamics, few such dynamical basis functions suffice to provide the required numerical accuracy \([7,8]\). The major computational advantage is lost in these approaches however, since the number of such basis functions increases exponentially with the number of degrees of freedom in the system.

1.3. QUANTUM MECHANICAL METHODS.

1.3a. The time dependent self consistent field method (TDSCF).

We first discuss the TDSCF approach \([11]\) which is based on the time dependent variational principle \([12]\) and is free from divergences. The trial wavefunction in this theory is taken as a product of wave packets which depend on a single degree of freedom i.e.,

\[
\psi (r) = \prod_i \phi_i (r_i) \exp (i\theta t), \quad (1.3.1)
\]
where $\phi (r)$ are the wave packets dependent on a single degree of freedom $r$ and $\delta$ is the overall time dependent phase factor. The general hamiltonian of a many particle system can be written as

$$H = \sum h_i + V$$

(1.3.2)

where $h$ correspond to the $i$th degree of freedom and $V$ is the interaction potential. We now apply the time dependent variational principle according to which

$$\delta \psi \int \left< \psi ; H - i \phi / \partial t ; \psi \right> dt' = 0$$

(1.3.3)

Substituting the equations for the hamiltonian and the wave function in the above equation gives

$$\delta \phi_i \int \left< \prod \phi_i (r_i) ; \sum h_i + V - i \phi / \partial t ; \prod \phi_j (r_j) \right> dt' = 0$$

(1.3.4)

From the above integral the following equations emerge.

$$i \phi_i (r_i) = h_i^{scf} \phi_i$$

(1.3.5)

where,

$$h_i = \sum h_i + \int \prod_{j \neq i} \phi_j^* (r_j) V \phi_j (r_j) \, dr_j$$

(1.3.6)

In this approximation, the potential elements are counted twice i.e., $\phi_i (r_i)$ interacting with $\phi_i (r_i)$ and vice versa. To account
for this error a term is subtracted from the phase factor of the wave function which is given by

$$\theta = \int \prod \phi^*_j (r_j) \wedge \phi_j (r_j) \, dr_j.$$  \hspace{1cm} (1.3.7)

The above three equations are the TDSCF equations which are solved self-consistently to obtain the required properties of a system. This approach is size-consistent and size-extensive and has been applied to the calculation of dynamics of molecular collisions, molecular absorption spectra and non-adiabatic dynamics [12].

The TDSCF is an approximation to the exact dynamics and its wave packet deviates from the exact wave function as the time progresses. Two approaches, the Configuration Interaction (CI) based on TDSCF orbitals [12a] and the MCTDSCF [12b] have been discussed in literature to go beyond TDSCF. In this sense the TDSCF provides a recipe to generate the dynamical basis to carry out the CI calculations. It has been shown that the number of functions required to achieve convergence is quite small in these approaches. However, these methods also suffer from the exponential growth of the basis with the number of degrees of freedom.

1.3b. The time dependent coupled cluster method (TDCCM).

Unlike the methods described above, the time dependent coupled cluster method [13-18] is based on the operator solution to the time dependent Schrödinger equation in which the part of
the evolution operator that generates the component of the wave function outside the chosen model space is written as an exponential operator.

\[ |\psi> = \exp (S) |0> \]  \hspace{1cm} (1.3.8)

We now summarise some of the works that appeared in literature on TDCCM.

The formulation of the TDCCM has appeared in the late seventies. Schonhammer and Gunnarson [13] introduced the time dependent generalisation of the coupled cluster method to calculate the spectral functions of fermi systems. They parametrise the wave function as

\[ |\phi(t)> = N(t) \exp (S(t)) |\phi_0> \]  \hspace{1cm} (1.3.9)

where \( N(t) \) is a normalisation factor and \( S(t) \) is a time dependent operator creating particle-hole pairs with respect to the state \( |\phi_0> \).

\[ S(t) = \sum a_{am} (t) \psi_a^+ \psi_m + \sum a_{abmv} (t) \psi_a^+ \psi_b^+ \psi_m \psi_v + \ldots \]

\[ = \sum_{n=1}^{\infty} S^{(n)} (t), \]  \hspace{1cm} (1.3.10)

where \( \psi \) are the annihilators of the singly occupied particle states in \( |\phi_0> \) and \( a \psi \) are the creation operators of the unoccupied single particle states in \( |\phi_0> \). \( S(t) \) satisfy the condition
As the spectral function is determined by $\langle \phi_0^\dagger \phi_0 \rangle$, which can be rewritten as

$$\langle \phi_0^\dagger \phi_0 \rangle = N(t),$$

their interest is to determine $N(t)$ which they do so by substituting eq (1.3.9) in the time dependent Schroedinger equation given by

$$i \psi = H \psi(t).$$

Hence the following equation is obtained

$$i \left( \frac{\dot{N}(t) + \dot{S}(t) N(t)}{S(t)} \right) \exp (S(t)) \phi_0 = N(t) H \exp (S(t)) \phi_0$$

Premultiplying the above equation with $\exp(-S)$ amounts to

$$i \left( \frac{\dot{N}(t) + \dot{S}(t) N(t)}{S(t)} \right) \phi_0 = N(t) \bar{H}(t) \phi_0$$

where

$$\bar{H}(t) \phi_0 = \exp (-S(t)) H \exp (S(t))$$

Projecting eq(3) on the left with $\phi_0$ gives the equation for $N(t)$ and $S^n(t)$ as

$$i \dot{N}(t) = N(t) \langle \phi_0^\dagger \bar{H}(t) \phi_0 \rangle$$
The above formalism is applied to include only the first term in \( S(t) \) involving \( \psi_y \).

Hoodbhoy and Negele (14] have applied the time dependent formalism to the CCM and specified the truncations appropriate to potentials with strongly repulsive cores.

Arponen later introduced a biexponential operator to describe the wave operator [15] leading to two different ways of obtaining the CCM equations and then extended it to derive the time dependent equations. The main attraction of this procedure is that the expectation value of an operator can be determined in a straightforward manner. We describe the method in the following discussion.

As is known the CCM wave function of the ground state is given by

\[
|\psi\rangle = \exp(S) |\phi\rangle, \quad (1.3.20a)
\]

\[
\langle \psi | \psi \rangle = \langle \phi | \exp(S) \rangle, \quad (1.3.20b)
\]

where \(|\phi\rangle\) is the noninteracting ground state. \( S \) is expanded as

\[
S = \sum S_i c_i^+, \quad (1.3.21)
\]

\[
S' = \sum S'_i c_i^+, \quad (1.3.22)
\]
where $c.$ and $c.$ are respectively the excitation and deexcitation operators with respect to $\phi$ and $S$ and $S$ are the numerical amplitudes. The energy eigenvalue equation is given as

$$H \exp(S) |\phi\rangle = E \exp(S) |\phi\rangle \quad (1.3.23)$$

Left multiplying by $\exp(-S)$ gives

$$\exp(-S) H \exp(S) |\phi\rangle = E |\phi\rangle \quad (1.3.24a)$$

$$H |\phi\rangle = E |\phi\rangle \quad (1.3.24b)$$

The transformation to $H$ is not unitary and hence it is not hermitian. The expectation value of an operator can be written as

$$\langle A \rangle = \langle \phi | \exp(S) \cdot A \cdot \exp(S) |\phi \rangle / \langle \phi | \exp(S) \exp(S) |\phi \rangle$$

$$\quad (1.3.25)$$

Introducing the notation

$$\langle w \rangle = \langle \phi | \exp(S) \exp(S) / \langle \phi | \exp(S) \exp(S) |\phi \rangle \quad (1.3.26)$$

one obtains

$$\langle A \rangle = \langle w \rangle \langle A \rangle |\phi \rangle \quad (1.3.27)$$

Applying the linked cluster theorem the equation for $\langle w \rangle$ becomes

$$\langle w \rangle = \langle \phi | \exp(S) \quad (1.3.28)$$
where
\[ S = \sum S_i c_i \tag{1.3.29} \]

Equations (1.3.27) and (1.3.28) imply that \( \langle A \rangle \) is of finite order if \( S \) and \( S' \) are truncated at some finite order \( n \). At this stage a new energy functional is defined in which the similarity transformation is performed using a product of two exponentials \( \exp(S)\exp(S') \).

\[
T[ S, 0] = \langle \phi \mid 0 \exp(-S) \mathbf{H} \exp(S) \mid \phi \rangle \tag{1.3.30}
\]
where
\[
0 = \exp(S) \tag{1.3.31}
\]
and
\[
\langle \upsilon \mid = \exp(S) \exp(S') \langle \phi \rangle \tag{1.3.32}
\]

An alternative way of writing this functional is

\[
T[ S, S'] = \langle \phi \mid \exp(S) \exp(-S) \mathbf{H} \exp(S) \mid \phi \rangle \tag{1.3.33}
\]

Two different truncations are obtained by applying the variational principle to the variable parameters \( 0. \) and \( S \).

\[
a T/ \partial 0 = \langle \phi \mid c, \mathbf{H} \mid \phi \rangle = 0, \tag{1.3.34}
\]
\[
a T/ \partial S_i = \langle \phi \mid 0| \mathbf{H}, c^+ \mid \phi \rangle = 0, \tag{1.3.35}
\]

from which the coefficients \( c_1 \) and \( c_2 \) are obtained.

The time dependence of the cluster amplitudes \( S \) and \( S' \) is obtained by applying the time dependent variational principle.
which is described in the following discussion. Consider the

functional

\[ A(t | \psi, \psi' \rangle = \int \frac{dt}{v(t)} : [ i \partial/\partial t - H(t) ] \psi(t) \]  \hspace{1cm} (1.3.36) \]

applying the double exponential form for \( |\psi(t)\rangle \) we obtain

\[
A [S, S'] = \int dt < \phi \left| e^{S'(t)} e^{-S(t)} [ i \partial/\partial t - H(t) ] e^{S(t)} \right| \phi > \\
\quad = \int dt < \phi \left| e^{S'(t)} e^{S(t)} \right| \phi > - \int dt T(t)  \hspace{1cm} (1.3.37)
\]

The working equations of motion are obtained by imposing that \( A \) is stationary with respect to changes in \( S \) and \( S' \). Hence, the equations of motion for the cluster amplitudes are obtained to be

\[
i \sum_j K_{ij} \dot{S_j} = \sigma T/ \partial S_i. \hspace{1cm} (1.3.38a)
\]

\[
i \sum_j \dot{S'}_j K_{ji} = \sigma T/ \partial S_i. \hspace{1cm} (1.3.38b)
\]

where

\[
K_{ij} [S''_i] = < \phi \left| c_i \exp (S'') c_j^+ \right| \phi > \hspace{1cm} (1.3.38c)
\]

\( K, S \) and \( T \) are all time dependent quantities.

In summary, two features distinguish Arponen's theory. First he uses a biexponential ansatz to represent the wave operator. Second a variational procedure is used to determine the cluster amplitudes. The approach is restricted to closed shell systems however and extensions to multideterminental reference functions are not trivial.
Ion-neutralisation scattering from surfaces was studied by Sebastian [16] using the time dependent formalism so that electron correlation is explicitly included to describe the process accurately. The wave function is assumed to have the form

\[ |\psi(t)\rangle = \exp\{T_1(t) + T_2(t) + T_3(t) + \ldots\} |\phi_0\rangle \]

where \( \phi_0 \) is a slater determinant and \( T(t) \) can create \( n \)-particle hole excitations in it. \( T(t) \) contains single particle hole-excitation operators and \( T_2(t) \) contains those two-particle hole-excitation operators which transfer two electrons to the ion from the solid surface. He neglected all the \( T(t) \) for \( n > 2 \). Substituting for \( |\psi(t)\rangle \) in the time dependent Schroedinger equation, the equation for \( T(t) \) are obtained. The wave function is approximated as

\[ \langle \psi(t)| = \exp\{T_0(t) + T_1(t)\} \{1 + T_2(t)\} |\phi_0\rangle \]

It was shown that TDCCM at this level of approximation is adequate to describe the electron transfer processes accurately.

The time dependent coupled cluster method for the propagation of harmonic oscillator vacuum states (gaussians) on multidimensional anharmonic surfaces has been developed by Durga Prasad [17]. Using the exponential of creation operators as the time evolution operator, the calculation of molecular absorption spectra was shown. The molecular vibrational hamiltonian is taken to be
\[
H(\alpha) = E_\alpha + \sum_{i} w_i(\alpha) a_i^\dagger a_i + \sum_{i<j} V_{ij}(\alpha) (a_i^\dagger a_j^\dagger) + \ldots \ldots
\]  

(1.3.41)

where \( \alpha \) represents the index of the electronic state and \( E_\alpha \) is the vertical excitation energy, \( w_i \) are the frequencies, \( V \) are the anharmonic coupling constants and \( a_i^\dagger \) and \( a_i \) are the harmonic oscillator ladder operators corresponding to the mode \( i \). The ground state is taken to be the vacuum state on the assumption that the anharmonic terms do not effect the vibrationless state of the lower electronic state. Hence,

\[
|\phi_g\rangle = |0\rangle.
\]  

(1.3.42)

The time evolution operator is parametrised in the Wei-Norman [20] product form and arranging it in normal order as

\[
U |0\rangle = \exp \{ S \} |0\rangle
\]  

(1.3.43)

where

\[
S = S_0 + S_1 + S_2 + S_3 + \ldots \ldots
\]  

(1.3.44a)

\[
S_1 = \sum_i s_i a_i^\dagger
\]  

(1.3.44b)

\[
S = 1/2! \sum_{i<j} s_{ij} a_i^\dagger a_j^\dagger + \ldots \ldots
\]  

(1.3.44c)

and so on. The annihilation operators are not included as in the normally ordered form they are to the right and acting on \( |0\rangle \) would give zero. The wave function at a given time \( t \) is given by

\[
|t\rangle = \exp \{ S \} |0\rangle.
\]  

(1.3.45)
The equations for the cluster amplitudes $S_e$ are obtained by substituting eq. (1.3.45) in the time dependent \textit{Schroedinger} equation given by

$$i \frac{d}{dt} \mid t \rangle = H_e \mid t \rangle$$ \hfill (1.3.46)

Premultiplying by $\exp(-S)$ we get

$$i \exp(-S) \frac{d}{dt} \exp(S) \mid 0 \rangle = \exp(-S) H \exp(S) \mid 0 \rangle$$ \hfill (1.3.47)

projecting on to different excited states $\mid m \rangle$ we obtain

$$i \mid s \rangle = \langle m \mid \bar{H}_e \mid 0 \rangle,$$ \hfill (1.3.48)

where

$$\bar{H}_e = \exp(-S) H_e \exp(S),$$ \hfill (1.3.49)

which are coupled \textit{non-linear} differential equations that are integrated by using the initial condition

$$s_m(0) = 0$$ \hfill (1.3.50)

The fourier transform of $\exp(S_\infty)$ gives the spectrum. This formalism was applied to evaluate the absorption spectra of the two dimensional \textit{Henon-Heils} hamiltonian.

The time dependent coupled cluster formalism with a \textit{multireference model} space was presented by Guha and Mukherjee \cite{18}. Similar to Arponen's formalism, their work is inspired by the analysis of many body perturbation theory. The time dependent
non-stationary functions \( \psi_k(t) \) at some initial time \( t_0 \) are built as a linear combination of a set of strongly interacting time independent functions belonging to a model space \( M \).

\[
\psi_k(t_0) = \sum c_{1k} \phi_i \quad (1.3.51)
\]

The time evolution of \( \psi_k \) is given by

\[
\psi_k(t) = U(t,t_0) \psi_k(t_0), \quad (1.3.52)
\]

where \( U(t,t_0) \) satisfies the equation

\[
i\hbar U(t,t_0)/\partial t = H(t) U(t,t_0). \quad (1.3.53)
\]

A model evolution operator \( U_m \) and a model time dependent effective hamiltonian \( H_{\text{eff}} \) are defined in the model space via

\[
\psi_k^0(t) = U_m(t,t_0) \psi_k^0(t_0) \quad (1.3.54)
\]

\[
i\hbar U_m(t,t_0)/\partial t = H_{\text{eff}}(t) U_m(t,t_0) \quad (1.3.55)
\]

The evolution is factorised as

\[
U_P = U_{\text{ex}} U_m P \quad (1.3.56)
\]

where \( P \) describes the projection on to model space and \( U \) is the evolution operator defined in the complementary space.

Substituting eq. (1.3.56) in eq. (1.3.53)
The PP component is given by

\[ \frac{i\partial U_{ex}}{\partial t} = HU_{ex} - U_{ex} H_{eff} \quad (1.3.57) \]

The evolution of \( \mathbf{U}^Q \) where \( Q \) defines the projection on to virtual space is given by

\[ \frac{i\partial U_{ex}^Q}{\partial t} = [H U_{ex}]^Q - U_{ex}^Q H_{eff} \quad (1.3.59) \]

The equation for \( \mathbf{U} \) and \( \mathbf{U}_n \) are decoupled as \( H_{eff} \) depends only on \( U \). Hence, \( H_{eff} \) is solved from eq.(1.3.58) and substituting in eq. (1.3.55) \( U_n \) is obtained. The two evolution operators are defined as \( U_M \) and \( U_M \)

\[ U_M = \{ \exp [X] \} \quad (1.3.60) \]

\[ U_{ex} = \{ \exp [S] \} \quad (1.3.61) \]

\( X \) defines closed operators (closed operators which cause transitions within the model space) and indicate normally ordered products. Although in principle \( S \) contains closed operators as well as external operators (external operators cause transitions from the model space to the virtual space), it is sufficient to have only external operators in it. Substituting \( U \) in eq.(1.3.59) and rewriting in normal order gives
\[ \frac{i\partial S}{\partial t} \mid _{\text{ex}} = \overline{H} U_{\text{ex}} - U_{\text{ex}} \overline{H}_{\text{eff}} \]  

(1.3.62)

The bar on the top indicates connected diagrams. Considering the closed part of the above equation \( S = 0 \) gives

\[ \{ \overline{U}_{\text{ex}} \}_c_{\text{l}} \overline{H}_{\text{eff}} = \{ \overline{H} U_{\text{ex}} \}_c_{\text{l}} \]  

(1.3.63)

Similarly with the external pair

\[ i\frac{\partial S}{\partial t} = \{ \overline{H} U_{\text{ex}} \}_c_{\text{l}} - \{ U_{\text{ex}} \overline{H}_{\text{eff}} \}_c_{\text{l}} \]  

(1.3.64)

The equation for \( X \) is

\[ i\frac{\partial X}{\partial t} = \{ \overline{H}_{\text{eff}} U_{\text{ex}} \}_c_{\text{l}} \]  

(1.3.65)

The above two equations are the working equations in this formalism. This formalism was applied to a three dimensional rotated harmonic oscillator.

1.3c. The Lie-algebraic approach.

Another method which received attention in recent years is the Lie-algebraic method \([19-24, 26-35]\). The essential feature of the algebraic approaches is the realization that if the Hamiltonian is an element of a Lie-algebra,

\[ H = \sum_i h_i l_i \]  

(1.3.66)
\[ \{ l_i, l_j \} = \sum_k C^k_{ij} l_k \]  

(1.3.67)

The time evolution operator can be parametrized as the exponential of an antihermitian element of that algebra.

\[ U = \exp(X), \]  

(1.3.68)

\[ X = -X^+ = \sum_i x_i l_i. \]  

(1.3.69)

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 into the Schroedinger's equation for the evolution operator

\[ i U^{-1} \dot{U} = U^{-1} H U. \]  

(1.3.70)

Expanding both sides of eq. (1.3.70) by the well known Hausdorff expansion [21] and equating the coefficients of each \( l \) on either side of the equation provides the required working equations. The resulting expressions are compact and provide a convenient route for generating the time evolution operator either perturbatively as is done in Magnus expansion or non perturbatively.

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 \textit{di}mensional. The most general class of \textit{hamiltonian}s that belong to a finite \textit{di}mensional Lie-algebra, other than the projection operator algebra operative in finite dimensional vector spaces, are the quadratic \textit{hamiltonian}s. Consequently, a large body of studies have appeared in which quadratic \textit{hamiltonian}s which belong to the harmonic oscillator algebra have been studied by the \textit{Lie-algebraic} method. We now discuss the application of the \textit{Lie-algebraic} methods by various authors.

Pechukas and Light [22] discuss the Magnus [19] formula for the exponential \textit{representation} of the operator solution to the Schroedinger equation for a time dependent \textit{hamiltonian} to obtain a unitary time evolution operator. The time evolution of a system at time $t = t_0$ described by a wave function $\psi(t_0)$ is given by the TDSE

$$i\hbar \frac{\partial U(t,t_0)}{\partial t} = H(t) U(t,t_0),$$  \hfill (1.3.71)

where $U(t,t_0)$ is the time evolution operator. If the \textit{hamiltonian} of the system $H$ is described in the Schroedinger picture then $H$ becomes time independent and the above equation is easily integrated. On the contrary if $H$ is time dependent as in the interaction picture then the above equation which cannot be written as

$$U(t,t_0) = \exp \left\{ -i \int_{t_0}^{t} dt' \frac{H(t')}{\hbar} \right\}$$  \hfill (1.3.72)

Normally $U(t,t_0)$ is obtained by expanding it in a perturbation series obtained by \textit{iteratively} integrating eq. (1.3.72)
$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} dt_1 H(t_1) U(t_1, t_0)$ \hspace{1cm} (1.3.73)

$= 1 - \frac{i}{\hbar} \int_{t_0}^{t} dt_1 H(t_1) + \frac{(i/\hbar)^2}{2!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 H(t_1)H(t_2) + \cdots$ \hspace{1cm} (1.3.74)

$U(t, t_\infty)$ obtained by truncating the above series is not unitary. The exponential form of $U$ is very appropriate for a unitary transformation. One way of constructing $U(t, t_\infty)$ is to define an operator $A$ given by

$$\exp \left[ A(t) J = U(t, t_0) \right]$$ \hspace{1cm} (1.3.75)

such that $A$ is anti-hermitian. In that case $U$ becomes a unitary operator. Hence, $A$ which is a functional of $H$ has to be determined as shown by Magnus [19]. $A$ is expanded as a series in which the $n$th term is a sum of integrals of $n$-fold multiple commutators of $H(t')$. Each term in the series is itself anti-hermitian and hence one obtains a unitary representation irrespective of the point at which the truncation is made. Pechukas and Light applied the Magnus expansion to a harmonic oscillator with a time dependent force constant [22] and used the operators $[q, p, \{qp + pq\}]$ which form a Lie-algebra to define $A(t)$ as

$$A(t) = \alpha(t)q^2 + \beta(t)p^2 + \gamma(t)(qp + pq)$$ \hspace{1cm} (1.3.76)

Although the unitarity of the evolution operator is
maintained, the Magnus expansion is subjected to a few drawbacks. The theory being based on the perturbation series expansion of A, the governing equations of A also result in infinite series. Hence, no non-perturbative solution can be applied. Also under some conditions, the solutions to the equation may not exist. As the existence of a solution is questionable, Wei and Norman have [20] alternatively parametrised the evolution operator in a non-canonical product form of exponential operators given by

\[ U_w = \prod_k \exp(c_k L_k) \]  

(1.3.77)

They have shown that if the Lie-algebra to which the hamiltonian belongs is a solvable algebra then it is possible to order the elements of the algebra in such a way that global solutions to the evolution operator can be obtained. In case the lie-algebra from which the evolution operator is constructed is not simple then the equations of motion for the different sets coefficients can be decoupled by invoking a reduction principle.

The time evolution operator can also be constructed using the Levi -Malcev decomposition of a Lie-algebra which states that every finite dimensional Lie-algebra is the semidirect sum of its unique radical R and a semisimple subalgebra S. Invoking the Wei-Norman form for the time evolution operator U, U is written as [19]

\[ U = U_S U_R \]  

(1.3.79a)
and the **hamiltonian** is written as

\[ H = H_S + H_R. \]  

(1.3.79b)

Substituting the above two equations in the TDSE, decoupled equations of motion are obtained i.e,

\[ i \frac{dU_S}{dt} = H_S U_S, \]  

(1.3.80a)

\[ i \frac{dU_R}{dt} = (U_S^{-1} H_R U_S) U_R. \]  

(1.3.80b)

The **semisimple** algebra can be directly decomposed as a direct sum of simple ideals [20b]

\[ S = S_1 \oplus \ldots \ldots \oplus S_k. \]  

(1.3.81a)

Hence \( U_c \) is parametrised as

\[ U = U_1 U_2 \ldots U_k. \]  

(1.3.81b)

Equation (1.3.80a) now reduces to solving smaller subordinate problems

\[ i \frac{dU_k}{dt} = H_k U_k, \]  

(1.3.82)

where \( H_1 \in S_1 \).

Another drawback of the Magnus expansion is that the
perturbation series expansion breaks down in the presence of degeneracies. To account for this, degenerate perturbation theory has been invoked.

Sree latha and Durga Prasad [23] have alternatively parametrised the evolution operator in the Wei-Norman form using the projection operator algebra which is a simple algebra (in this sense different from the Wei-Norman requirement) by invoking a reduction principle to obtain decoupled equations of motion. The Lie-algebraic structure was classified as follows:

1) Set of excitation operators: \( E = \{ X = \langle v | \langle m \rangle \} \)
2) Set of deexcitation operators: \( D = \{ Y = \langle m | \rangle \langle v \rangle \} \)
3) Set of shift operators: \( S = \{ Z = \langle m | \langle n \rangle \}, W = \langle u | \rangle \langle v \rangle \} \)

where \( u, v \in V \) (virtual space) and \( m, n \in M \) (model space).

By invoking the reduction principle they arrived at the following time evolution operator

\[
U = \exp(X) \exp(Y) \exp(Z+W)
\]  

(1.3.78)

The resulting equations of motion are decoupled and contain finite order polynomials. They solved the equations of motion by applying perturbation theory.

Micha et al [24] have studied atom-diatom and diatom-diatom collision using the Lie-algebraic method. The Lie-algebraic structure they have utilized for their calculations contains the elements \( \{ q, q \hat{p} + q \hat{p}, p, q, \hat{p} \} \) in this order. The interaction potential is expanded as a Taylor series and truncated at the
quadratic level. As a consequence at most quadratic terms have to be retained in the *hamiltonian* \( H \) given by

\[
H(t) = H_0 + V
\]  
(1.3.83)

The *hamiltonian* is converted to the interaction picture *hamiltonian* \( H_I(t) \) given by

\[
H_I(t) = \exp [iH_0 t/\hbar] \left( \sum V(t) \right) \exp [-iH_0 t/\hbar] = \prod \sum f_n(t) x_n
\]  
(1.3.84)

where \( x \) are closed with respect to commutation and form a Lie-algebra. The evolution operator in the interaction picture is constructed as

\[
U_I(t,t_0) = \prod_{n=1}^6 \exp \left[ -i \alpha_n(t) x_n \right]
\]  
(1.3.85)

which satisfies the equation

\[
i\hbar \frac{d}{dt} U_I(t,t_0) = H_I(t) U_I(t,t_0)
\]  
(1.3.86)

Substituting the equations for \( U_I \) and \( H \) in the above equation results in the working equations for \( \alpha(t) \). Making the substitution,

\[
\alpha_1(t) = -P_1(t) / [2\xi Q_1(t)]
\]

results in two first order linear differential equations for \( Q_1 \).
and \( P \) which are solved to obtain \( P \) and \( Q_1 \) and in turn \( \alpha(t) \). As the equation for \( a_n(t) \) depends only on \( \alpha(t) \) and the equation for \( a_n(t) \) depends only on \( a_n(t) \), these equations are analytically solvable. Therefore solving for \( a_1, a_2, \) and \( a_3 \) requires solving only two differential equations for \( P \) and \( Q \). The rest of the differential equations have to be solved numerically. The attraction this procedure offers is that fewer number of equations need be solved to obtain the parameters \( a(t) \).

Calculations for linear and linear + quadratic potentials have been performed and the results were compared with the quantum mechanical results of Secrest and Johnson [25]. Potential containing linear + quadratic terms showed better agreement with the quantum mechanical results. Later on when they extended [26] this procedure to a two dimensional case involving diatom-diatom collision a completely Lie-algebraic theory could not be used.

The Hamiltonian was segregated into

\[
H(t) = H^{(1)}(t) + H^{(2)}(t) + V^{(12)}(t) \tag{1.3.88}
\]

where

\[
H^{(i)}(t) = H_0^{(i)} + F_i(t) q_i + \frac{1}{2} G_{ij}(t) q_i^2 \tag{1.3.89a}
\]

\[
V^{(12)}(t) = G_{12}(t) q_1 q_2 \tag{1.3.89b}
\]

and

\[
F_i(t) = \left( \frac{\partial V}{\partial q_i} \right)_{q_1=q_2=0} \tag{1.3.90a}
\]

\[
G_{ij}(t) = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{q_1=q_2=0} \tag{1.3.90b}
\]
The time evolution operator is similarly obtained in the interaction picture from

\[ U_I(t,t_0) = U_I^{(1)}(t,t_0) U_I^{(2)}(t,t_0) U_I^{(12)}(t,t_0) \]  \hspace{1cm} (1.3.91)

The differential equations for the interaction picture time evolution operator are given by

\[ i\hbar \frac{\partial U_I^{(j)}}{\partial t} = H_I^{(j)}(t) U_I^{(j)}(t,t_0) \]  \hspace{1cm} (1.3.92)

and

\[ i\hbar \frac{\partial U_I^{(12)}}{\partial t} = [ U_I^{(1)} + U_I^{(2)} + H_I^{(12)}(t) U_I^{(2)} U_I^{(1)} ] U_I^{(12)}(t,t_0) \]

\[ = V_I^{(12)}(t) U_I^{(12)}(t,t_0) \]  \hspace{1cm} (1.3.93)

The equations of motion for the system excluding the residual coupling \( V_I^{(12)}(t) \) are obtained as in the one-dimensional case. Because the set of operators occurring in the residual coupling, after applying the transformations of the above equations, do not commute, the algebraic theory cannot be applied here. Instead first order perturbation theory and basis set expansion methods were invoked to treat the residual coupling. The advantage of this procedure is that as the residual coupling contains only linear and bilinear terms in the interaction picture, the matrix in the basis set expansion is very sparse than the matrix obtained from expanding from the very beginning as in that case the matrix elements obtained from the quadratic terms also have to be evaluated. The basis set bottleneck still exists if terms higher than linear and bilinear are included in the residual
coupling or if more number of degrees of freedom are dealt with. The disadvantage of using perturbation theory is that for large residual coupling it fails. Hence, to account for this sequence of transformations were carried out which reduces the coupling at each step [27]. When the coupling becomes very small, perturbation theory is applied. The sequence of transformations are given by the following equations,

\[ V_c^{(k)} = \left( U_L^{(k-1)} \right)^+ V_{BL} U_L^{(k-1)} \]  
(1.3.94a)

\[ i\hbar \frac{\partial U^{(k)}_{BL}}{\partial t} = V_c^{(k+1)}(t) U^{(k)}_{BL}(t, t_0) \]  
(1.3.94b)

\[ U^{(k)}_{BL}(t_0, t_0) = 1 \]  
(1.3.94c)

where \( V \) is the residual coupling and the subscripts \( L \) and \( BL \) denote the linear and bilinear terms of the residual coupling respectively. The time evolution operator after each transformation is given by

\[ U^{(k)}_L = \exp \left[ -i\xi_1^{(k)} q_1 \right] \exp \left[ -i\eta_1^{(k)} p_1 \right] \exp \left[ -i\xi_2^{(k)} q_2 \right] \exp \left[ -i\eta_2^{(k)} p_2 \right] \]  
(1.3.95)

where \( \xi \) and \( \eta \) are time dependent coefficients. In general after the \( k \)th transformation the evolution operator \( U \) is given by

\[ U = U_1 U_2 U_L^{(0)} U_L^{(1)} U_L^{(2)} \ldots \ldots \ldots \ldots U_L^{(k)} U_{BL}^{(k)} \]  
(1.3.96)

In their calculations they carried out three transformations
(k=0,1,2) to reduce the coupling before they applied perturbation theory.

Shin [28] studied the coupling of VV and VT energy transfer modes in molecular collisions using the Lie-algebraic theory. VV and VT intermode coupling in vibrational energy transfer processes involving highly excited diatomic molecules were studied. Only the linear terms in the Hamiltonian were retained. The Hamiltonian contained the operators,

\[ \{ a_1^+ a_1, a_2^+ a_2, a_1^+, a_1^+, a_2^+, a_2^+, a_1^+ a_2, a_1 a_2^+ \}. \]

The terms containing \( a a \) and \( a_1 a_2 \) describe the VV energy exchange and the rest describe the VT energy transfer. The evolution operator was parametrised in terms of the operators contained in the Hamiltonian. The linear approximation to the potential was invoked to evaluate the transition probabilities for the collision of two identical molecules which simplifies the scattering equations of motion further. They also carried out calculations including the quadratic terms in the potential but the dimensionality of the problem reduced as the 1-dimensional Hamiltonian was considered.

Benjamin [29] applied the algebraic approach to the collision linear collision of an atom and a diatom and a diatom and a diatom. In the model he has treated the translational motion classically and vibrational motion quantum mechanically. The interaction potential in the Hamiltonian is expanded using a Taylor series expansion up to the quadratic level, about the classical orbit which is determined by solving the Hamilton's
equations of motion. He described three methods to tackle the problem and compared each of these methods. The first of these methods which he called QDPO (quadratically driven parametric oscillator) considers the full algebraic structure of a quadratic algebra \( a, a, a, a, a, a, I \) where \( a \) and \( a \) are the harmonic oscillator ladder operators. The evolution operator in the Wei-Norman form is parametrised as

\[
U(t) = \exp[Z_1 a^+ a] \exp[Z_2 a^{+2}] \exp[Z_3 a^+] \exp[Z_4 a] \\
\times \exp[Z_5 a^2] \exp[Z_6]. \tag{1.3.97}
\]

This equation is substituted in the time dependent Schroedinger equation (TDSE) to contain six differential equations. These equations along with the Hamilton's equations of motion describing the translational motion are solved together to obtain the transitional probabilities. The second method neglects the quadratic terms in the evolution operator and the corresponding evolution operator is given by

\[
U = \exp[Z_1 a^+ a] \exp[Z_2 a^+] \exp[Z_3 a] \exp[Z_4]. \tag{1.3.98}
\]

He calls this approach as the LDPO (linearly driven parametric oscillator). The third approach which he calls the QDSO (quadratically driven scaled oscillator) makes use of a canonical transformation such that the coefficients of \( a \) and \( a \) are eliminated from the hamiltonian at any given time. The hamiltonian is separated into two parts; one involving the linear and \( a \ a \) terms (\( H_0 \)) and the other involving the quadratic terms.
The unitary operator is chosen such that

\[ S = \exp[\beta (a^2 - a^2)] \quad (1.3.99) \]

and a canonical transformation of the Hamiltonian is carried out.

\[ S \left( H_1 + H_2 \right) S^{-1} = \tilde{H}_1 = A(t)a^+a + B(t) (a^+ + a) + C(t). \quad (1.3.100) \]

The Hamiltonian now consists of only linear terms. Similarly, the evolution U is approximated to involve only a a and a a terms and is mathematically identical to the evolution operator corresponding to the LDPO approach. This approximation holds good only when the change in the frequency of the oscillator over one period of the unperturbed oscillator is very much smaller than the frequency of the unperturbed oscillator. The results from all the three procedures were compared with the exact results and in general the QDPO approach performed better than the other two approaches with the QDSO coming next. The formalism was extended to the two mode case. One of the drawbacks of the formalism is that decoupled equations of motion are not obtained due to which the formalism cannot be easily extended to using higher algebras and to systems consisting of several degrees of freedom. Also, the method is applicable only when the Hamiltonian consists of at most quadratic terms. As stated above the QDSO approach is applicable only for very small frequencies of the oscillator although it offers much simpler mathematics and lesser computational effort than the QDPO approach.

Yuan and Gilmore [30] have described the structure of the...
The double photon algebra (quadratic algebra) is utilised for which they construct a matrix representation. The time evolution operator is constructed as

$$U(t) = \exp \left[ ra^+ + Ra^+2 \right] \exp i \nu (n + 1/2) + 6 I \exp [la + La \).$$  

The ground state expectation value is obtained from

$$<0 | U(t) | 0 > = \exp [\eta(t)/2 + \delta(t)]$$ (1.3.103)

and a squeezed state expectation value is obtained from

$$|rR > = \exp [ ra^+ + Ra^+2 ] | 0 > \exp (n/2 + \delta).$$ (1.3.104)

From the matrix representation for the time evolution operator, they construct a unitary S operator. The unitary requirement on $U(t)$ is enforced by placing constraints on the time dependent parameters that appear in $U(t)$. These constraints are determined by applying the disentangling theorems. The TDSE is then solved by using the matrix representation for the Hamiltonian and the time evolution operator i.e.,

$$\frac{d}{dt} M \{ U(t, t_0) \} = M \{ H(t) \} M \{ U(t, t_0) \}$$ (1.3.105)
where $M$ denotes the matrix representation. This equation is integrated to obtain a non-unitary representation of the S-matrix. Using the symmetry properties of the S-matrix elements, a unitary representation for the S-matrix is obtained. As the Hamiltonian is restricted to be quadratic, the time evolution operator as in the previous studies is constructed from the quadratic Lie-algebra.

Shi and Rabitz [31] applied the Lie-algebraic formalism to the parametric amplifier and the collinear collision of an atom with a Morse oscillator. The state of the system at time $t$ is defined as is normally done in the algebraic theory as

$$\psi(t) = \sum c_n(t) \mid \phi_n \rangle$$  \hspace{1cm} (1.3.106)

where $c$ are the time dependent complex variables, $\phi_n$ are a finite set of states in the m-dimensional Hilbert space and $U$ is defined as

$$U [l(t)] = \exp \{ i l(t) - L \}$$  \hspace{1cm} (1.3.107)

where $l(t)$ are time dependent parameters associated with the elements $L$ to which the Hamiltonian belongs. The time derivative of the state vector $\psi(t)$ is given by

$$\psi(t) = \sum (c_n(t) U [l(t)] + c_n(t) U [l(t)]^* \mid \phi_n \rangle \}$$  \hspace{1cm} (1.3.108)

where $U [l(t)]$ is determined by the Feynman's disentangling
method.

\[ U \{ l(t) \} = i \frac{\partial}{\partial t} l \exp \left[ i l_k(t) L_k \right]. \]  \hspace{1cm} (1.3.109)

The equations of motion are now obtained by applying the time dependent variational principle which states that

\[ \delta \int_{t_1}^{t_2} dt \{ i \hbar \langle \psi(t) | \dot{\psi}(t) \rangle - \langle \psi(t) | H(L) | \psi(t) \rangle \} = 0. \]  \hspace{1cm} (1.3.110)

This leads to a set of classical equations of motion for the group parameters \( l(t) \) which are coupled to the equations of motion for the coefficients \( c(t) \). In their application to the parametric amplifier, they have considered a model Hamiltonian containing linear, bilinear and diagonal terms

\[ \{ a_1^+ a_1, a_2^+ a_2, a_1^+ a_2^+ a_1^+ a_2, a_1 a_2, a_1^+, a_1, a_2^+, a_2 \} \]

and the evolution operator was approximated accordingly. When extending it to more complicated case of the collision of an atom with a Morse oscillator they do not use a completely algebraic approach. The Morse oscillator part of the Hamiltonian was treated by the basis set expansion method using Morse basis and the relative motion is treated semi-classically using the group transformations. This has a greater advantage over the GWP as their formalism has a greater flexibility as any kind of basis can be used appropriate to the system under study.

More recently Echave et al. [32] suggested an alternative to the exponential ansatz of the time evolution operator. These
Instead of the coefficients $x_i$ in the exponential ansatz, the mixing coefficients $y_{ij}$ are now to be determined so as to optimize the convergence in the above equation.

They construct the Hamiltonian in the interaction picture which is defined by an effective time dependent Hamiltonian. The effective Hamiltonian is obtained by expanding the potential energy function around a reference value of the coordinate. They go about doing this in the following way. In the first step they propose an effective Hamiltonian

$$ H_{\text{eff}} = \sum h_i x_i, \quad (1.3.113) $$

where $x_i$ belongs to the Lie-algebra $L$ to which the Hamiltonian belongs. The matrix elements of $H$ are given by

$$ (H_{\text{eff}})_{jk} = \langle x_j | H - H_{\text{eff}} | x_k \rangle, \quad (1.3.114) $$

where $x_i$ are given by
where \( x \) also belong to \( L \) and \( G \) are the functions of time satisfying linear equations of motion. Another matrix \( F_{ik} \) is defined as

\[
[x_j, H_{\text{eff}}] = \sum_{k=1}^{n} F_{jk} x_k.
\] (1.3.116)

Hence the matrix \( \mathbf{6} \) satisfies

\[
i\hbar \frac{\partial G}{\partial t} = F G,
\] (1.3.117)

\( \chi_k \) are related to the time dependent coefficients by

\[
\phi(t) = \sum c_k(t) \chi_k
\] (1.3.118)

where \( \phi(t) \) is related to the state of the system \( \psi(t) \) by

\[
\psi(t) = U_{\text{eff}}(t, t_0) \phi(t). \] (1.3.119)

Substituting the above equation in the TDSE equations for the expansion coefficients are obtained,

\[
i\hbar \frac{d\mathbf{C}}{dt} = \mathbf{H}_{\text{I}} \mathbf{C}. \] (1.3.120)

These equations together with the equation for \( G \) are solved
together to obtain the dynamics of the system.

Lin et al [331 have applied the six-dimensional quadratic Lie-algebra to study the scattering of $^4\text{He}$ and $^3\text{He}$ particles from the (001) face of LiF crystal. They use the time evolution operator of the form

$$U_{\alpha\beta}(t) = \exp \{ T_{\alpha\beta}(t) \}$$  \hspace{1cm} (1.3.121)

where

$$T_{\alpha\beta}(t) = -\frac{i}{\hbar} \left[ U_{\alpha\beta}^{(1)} \right] + U_{\alpha\beta}^{(2)} a^* + U_{\alpha\beta}^{(2)*} a + U_{\alpha\beta}^{(3)} a + U_{\alpha\beta}^{(4)} a^* + U_{\alpha\beta}^{(4)*} a^* \right].$$  \hspace{1cm} (1.3.122)

Similar to the other applications of the Lie-algebraic they have also applied the formalism by retaining only quadratic terms in the Hamiltonian in which the potential is truncated to second order.

The use of time dependent basis sets to solve the TDSE has been done by Kucar and Meyer [34]. They have defined the time dependent basis sets $\psi(x,t)$ as

$$\psi_n(x,t) = U(t) \phi_n(x)$$

$$= \prod_{k=1}^{m} \exp \left[ i \alpha_k(t) A_k \right] \phi_n(x)$$  \hspace{1cm} (1.3.123)

where $a$ are real variables and $A$ are hermitian operators. $\phi_n$ are time independent complete set of functions choosen according to convenience. The wave function is now written as

$$\Psi(x,t) = \sum_n a_n(t) \psi_n(x,t)$$
The effective hamiltonian is defined as

\[ H_{\text{eff}} = \bar{H} + \sum_{k=1}^{m} \alpha_k \bar{A}_k, \]  

where

\[ \bar{A}_k = \left( \prod_{l=1}^{k-1} \exp(i\alpha_l A_l) \right) \bar{A} \left( \prod_{l=1}^{k-1} \exp(i\alpha_l A_l) \right) \]  

and

\[ \bar{H} = U^+ \bar{H} U. \]  

The coefficients \( \alpha \) satisfy the equations of motion

\[ i \dot{a}_n = \sum_l \langle \phi_l | H_{\text{eff}} | \phi_l \rangle a_l. \]  

\( \alpha(t) \) are determined so that the convergence of \( \Psi(x,t) \) is optimal from the variational principle stating

\[ \sum_n (n + 1/2)^j |a_n| = \langle f | H_0^j | f \rangle = \min \]  

where \( j \) is a parameter defining the family of variational principles. For example for \( j=1 \) they define a \( G \) such that

\[ \langle \psi | U H_0 U^{-1} | \psi \rangle = \langle f | H_0 | f \rangle = G(\alpha, \psi). \]

According to the variational principle

\[ \partial G / \partial \alpha_k = 0 \]
from which they determine a . In their calculations, they use the harmonic oscillator eigenfunctions for \( \phi \) and A. form the elements of a Lie-algebra to which the hamiltonian belongs. The Lie-algebra which they have chosen spans the operators \( \{ 1, x, -p, x^2, xp, H \} \) where

\[
XP = \frac{1}{2} (xp + px) \tag{1.3.132}
\]

and

\[
H_0 = \frac{1}{2} (p^2 + q^2). \tag{1.3.133}
\]

The time evolution operator is chosen as

\[
U(t) = \exp (-ix_t p) \exp (ip_t x) \exp (ib_t x^2) \exp (ia_t XP) \exp (i\gamma_t H_0) \\
X \exp (i\delta_t)
\]

\[
\tag{1.3.134}
\]

hence the time dependent basis become

\[
\psi_n (x,t) = \exp \left[ a_t/2 + ib_t (x-x_t)^2 + ip_t (x-x_t) + i(n + 1/2)\gamma_t + i\delta_t \right] \\
X \phi_n \left( \exp(at) (x-x_t) \right) \]

\[
\tag{1.3.135}
\]

from which the equations of motion are obtained. In the limit of harmonic potentials, the equations of motion are similar to that obtained by Heller. They have applied the formalism to a quartic potential and a Morse oscillator in which the exponential involves six terms. They have derived the above equations for the multidimensional case also. Although the time dependent basis can be represented more efficiently than the time independent basis, the drawbacks in this formalism are major. This requires solving
for the coefficients appearing in constructing the time dependent basis additionally and the Hamiltonian matrix has to be constructed at every iteration. Also in the course of propagation the differential equations may go stiff.

A different approach to solve for the dynamics of any system using the Lie-algebraic approach was developed by Alhassid and Levine [35]. They have discussed the procedure of maximal entropy which requires the initial state to be one of maximum entropy among all the states, consistent with a given set of constraints. These constraints are the expectation values of observables $A$ which are obtained from the available experimental data. The average value of the operator $A$ is given by

$$< A > = \text{Tr} (p \, A), \quad (1.3.136)$$

where $p$ is the density operator. The entropy corresponding to the state defined by $p$ is $S(p)$ given by

$$S(p) = -\text{Tr} (p \, \ln p). \quad (1.3.137)$$

The state of maximal entropy corresponds to

$$\rho = \exp \left\{ -\sum_{\tau=0}^{n} \lambda_{\tau} \, A_{\tau} \right\} \quad (1.3.138)$$

where $A$ are linearly independent observables and need not commute. $\lambda$ are constants to be determined (Lagrange's parameters) from the $n+1$ conditions given by

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Substituting the normalisation condition in the equation for $p$

$$\exp (\lambda_0) = \text{Tr} \left[ \exp \left( -\sum_{r=1}^{n} \lambda_r A_r \right) \right]$$

(1.3.140)

only when the sum in the above equation converges does the normalised density operator of maximal entropy exists. The $S [\rho]$ at the maximum is

$$S [\rho] = \lambda_0 + \sum_{r=1}^{n} \lambda_r \langle A_r \rangle.$$  

(1.3.141)

If $A$ commute it corresponds to the classical limit. The initial state being specified the functional form of the density operator is now determined from

$$-\ln \rho (t) = \sum_{r=0}^{\infty} \lambda_r (t) A_r.$$  

(1.3.142)

$A$ being known, $X$ are to be determined to obtain $p$. This is achieved by considering the time evolution of the density operator given by

$$\rho(t) = U(t, t_0) \rho(t_0) U^+ (t, t_0).$$  

(1.3.143)

The equations of motion are
\[ i \hbar \partial U(t, t_0)/\partial t = H U(t, t_0) \]  \hspace{1cm} (1.3.144a)

\[ i \hbar \partial \rho(t)/\partial t = [ H, \rho(t) ] . \]  \hspace{1cm} (1.3.144b)

Due to the unitarity of \( U \) the above equation holds good for \( \ln \rho(t) \) also.

\[ i \hbar \partial \ln \rho(t)/\partial t = [ H, \ln \rho(t) ] . \]  \hspace{1cm} (1.3.145)

The surprisal \( I \) which is the negative logarithm of density is now expanded as a linear combination of the Lie-elements.

\[ I = -\ln \rho \]  \hspace{1cm} (1.3.146)

where,

\[ I = \sum \lambda_r A_r \]  \hspace{1cm} (1.3.147)

where \( A \) are the Lie-elements and \( \lambda \) are constants. The equations of motion are obtained from

\[ i \dot{I} = [ H, S ] . \]  \hspace{1cm} (1.3.148)

Substituting the equation for \( I \) in the above equation results in

\[ i \sum \lambda_r A_r = \sum \{ H, A_r, \lambda_r \} \]

\[ = \sum \lambda_r \{ H, A_r \} . \]  \hspace{1cm} (1.3.149)

Let
Hence,

\[ [H, A_r] = \sum A_s G_{sr} \]

As \( A \) at the initial time are known, starting with this set of constraints the additional operators are added until the set of sufficient number of constraints are obtained subjected to the condition that these operators are closed under commutation with the Hamiltonian \( H \). This method is variational and can be taken to exact limits but for large systems where the constraints are many, the application of the formalism to get accurate results becomes difficult. They have applied this formalism to the linearly displaced harmonic oscillator in which the use of the six dimensional quadratic Lie-algebra has been made and the time evolution operator is taken as the exponential of linear combination of these elements (not the Wei-Norman form).

1.4. The Scope of the present investigation:

As can be seen from the discussion above, most of the algebraic approaches that have appeared to date utilize the harmonic oscillator algebra to construct a convenient dynamical basis in terms of which the dynamical calculations are carried out. In contrast, we attempt the construction of the time
evolution operator on anharmonic potential energy surfaces by considering the Lie-algebra of such Hamiltonians without invoking any basis sets at any stage of its construction.

The construction of the time evolution operator for anharmonic oscillators is discussed in chapter 1. For simplicity we first discuss the one-dimensional system and later extend it to the multidimensional case. The most general form of the one-dimensional Hamiltonian in such a case is

\[
H = \frac{p^2}{2m} + \sum_{n=0}^{\infty} \frac{1}{n!} V_n q^n. \tag{1.4.1a}
\]

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. This Hamiltonian is an element of the infinite-dimensional Lie-algebra

\[
L_0 = \{ Q_{mn} = q^m p^n ; 0 \leq m, n \leq \infty \} \tag{1.4.2a}
\]

Transforming to the harmonic oscillator ladder operator representation, we have

\[
H = \sum_{m,n} h_{mn} a^+ a \tag{1.4.1b}
\]

Here \( a \) and \( a^+ \) are the usual harmonic oscillator ladder operators defined as

\[
a^+ = \left( m \omega q + i (1/m\omega) p \right)/\sqrt{2} \hbar
\]
where $\omega$ is an arbitrary parameter. In this representation $L$ is given by

$$L_0 = \{ A_{mn} = a^m a^n ; 0 \leq m,n \leq \infty \}. \quad (1.4.2b)$$

Given that $H$ is an element of $L_0$, we can parametrize the evolution operator $U$ as

$$U = \exp[S] \quad (1.4.3a)$$

$$S = \sum_{m,n=0}^{\infty} S_{mn} a^m a^n ; \quad S_{mn} = -S_{nm}^*. \quad (1.4.3b)$$

This representation runs into two difficulties. To begin with, even when the summation for $S$ operator in eq(1.4.3) is restricted to some finite values of $m$ and $n$ ($m,n \geq 2$), the Hausdorff expansion gives a non-terminating series. The second problem with the representation (1.4.3) is that under some conditions the governing equations are not well defined. Both these problems arise because the ansatz (1.4.3) 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 Chapter 2 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 $L_0$. Two ways of decomposing the infinite dimensional lie-algebra are considered from which the time evolution operators for a general anharmonic hamiltonian are constructed. It is seen that for the vacuum state propagation these evolution operators correspond to the generalisations of the Normal Coupled Cluster method (NCCM) and the Extended Coupled Coupled Cluster method (ECCM) formalism of the coupled cluster theory discussed by Arponen [15]. The main advantage of invoking this reduction principle is that decoupled equations of motion are obtained. Extensions to multidimensional anharmonic oscillators AHOs will also be presented in chapter 2.

Convergence properties of the TDCCM applied to one dimensional potential energy surfaces are studied in chapter 3 and compared with the standard basis set expansion approach and for a better understanding of the applicability of the theory. Studies on exponentially repulsive, Morse potentials as well as atom-diatom collisions in the classical path approximation have been carried out for this purpose.

In chapter 4, the time dependent coupled cluster method (TDCCM) has been applied to the photodissociation dynamics of triatomic molecules within the framework of the Beswick and Jortner model [10] and a two dimensional Benon-Heils hamiltonian. Autocorrelation function and absorption spectra for the photodissociation dynamics have been evaluated and the convergence of the method has been tested by evaluating the autocorrelation function at different truncations of the S-matrix
elements. The norm conservation in the TDCCM applied to the 
Henon-Heils system is studied and the Franck-Condon spectra 
are obtained for a few mode) systems.

The algebraic approach has been applied to calculate the 
dynamics of a few model non-adiabatic single mode systems and 
model multi mode systems in chapter 5. To circumvent the problems 
arising in defining the initial conditions and the potential 
surface for such systems in this formalism, we have constructed a 
new hamiltonian which is derived by mapping the original 
hamiltonian on to a single electronic surface. Applications to a 
few model and realistic systems have been discussed. Later we 
extend the application of the algebraic approach to the complete 
non-adiabatic hamiltonian (without mapping) in the open shell 
formalism. Application to some realistic systems have also been 
discussed in this chapter.
REFERENCES