CHAPTER I

INTRODUCTION
Interpretation of properties of matter is a challenging field of fundamental interest for scientists. The analysis of macroscopic properties of a bulk system requires the understanding dynamical behaviour of the system at the molecular level i.e. molecular dynamics of the system.\textsuperscript{1} The substantial development in instrumentation and spectroscopic techniques has created a need for the development of theoretical methods to provide proper description of molecular dynamics. There are many theoretical methods developed till date for molecular dynamics studies. The standard approaches for obtaining such dynamics are (a) classical trajectory methods (b) semi-classical methods and (c) quantum mechanical methods.

Quantum effects such as the influence of zero point motion and the tunneling effect etc. are extremely important for certain dynamical events at the molecular level. Classical and \textit{semiclassical} methods cannot always provide a proper description of such processes. In this context, several quantum mechanical approaches have been developed for describing the dynamics of many particle systems.\textsuperscript{2} One can obtain the quantum dynamics in two ways: one is the time-independent approach and the other time-dependent approach. Basically the \textit{time-independent} or the time-dependent Schroedinger equation is solved respectively in the time-independent and time-dependent approaches.

The time-independent approaches\textsuperscript{4} require all \textbf{the eigenvalues} and \textbf{eigenstates} of the \textbf{hamiltonian} of the system considered and hence involve the construction and diagonalisation of large matrices. In certain conditions the time-dependent approaches are computationally faster. They are initial value
problems and so are often easier to implement. They are becoming increasingly popular due to their applicability to non-fully resolved experiments such as low resolution absorption, Raman spectroscopy and scattering. The other important processes in which the time-dependent approaches are applicable in obtaining the quantum dynamics are transition state spectroscopy, intramolecular energy transfer and collision dynamics in molecular beams. Noteworthy among the advantages these approaches offer are the ability to treat high level densities and the intuitive picture they provide for the physical process under study. Similarly description of externally driven systems requires the solution of time dependent Schroedinger equation. In relevance to our work a brief review on time-dependent approaches that are currently in vogue is presented here.

In the TD approaches the hamiltonian $H$ determines the time evolution of the system according to the Time-Dependent Schroedinger Equation (TDSE),

$$i\hbar \frac{\partial}{\partial t} \psi = H \psi.$$ \hspace{1cm} (1.0.1)

The time evolution of the wave function can also be represented as

$$\psi(t) = U(t,t_0) \psi(t_0),$$ \hspace{1cm} (1.0.2)

$$U(t_0,t_0) = 1,$$ \hspace{1cm} (1.0.3)

where $U(t,t)$ is the evolution operator which describes the
evolution of one vector in the Hilbert space into others. Substituting these equations in TDSE gives

\[ \text{ih} \frac{\partial U(t, t_0)}{\partial t} = H U(t, t_0) . \quad (1.0.4) \]

Obtaining the **dynamics** requires the solution of either eq.(1.0.1) or eq.(1.0.4). Several methods have been discussed in literature for the purpose. They can be classified broadly as (1) perturbative, (2) variational and (3) nonperturbative methods.

1.1 **PERTURBATIVE APPROACHES**

In the perturbative approaches \( H \) is generally written as

\[ H = H_0 + V(t) , \quad (1.1.1) \]

where \( H \) is part of the **hamiltonian** whose solutions are known and \( V(t) \) is the perturbation.

In the time-dependent perturbative methods, the evolution operator form of TDSE (eq.(1.0.4)) is considered and \( U \) is expanded as a power series in \( V \). Depending on the construction of \( U(t, t) \) these approaches can be subdivided into: (1) Dyson perturbation theory,\(^6,7\) (2) exponential perturbation theory,\(^8,16\) (3) degenerate perturbation theory.\(^17,19\) In addition, it is possible to use either stationary basis or dynamical **basis**\(^20,21\) to define the Hilbert space of interest.
1.1.1 Dyson Perturbation Theory:

Using the solutions of $H$ the wave function and the operators of the Hilbert space can be written down in a interaction picture frame. In the interaction picture the wave function is written as $\exp(-iHt)\psi(t)$ and the interaction hamiltonian is written as

$$H_1 = \exp(iH_0 t) \ V(t) \ \exp(-iH_0 t). \quad (1.1.2)$$

In this picture the evolution operator is denoted by $U$. The TDSE in this representation is

$$i\hbar \ a \ U_1(t,t_0) /a \ t = H_1 \ U_1(t,t_0). \quad (1.1.3)$$

$U$ is now expanded as a power series of $H$

$$U_1(t,t_0) = U_1^{(0)}(t,t_0) + \sum_{i=1}^{\infty} U_1^{(i)}(t,t_0), \quad (1.1.4a)$$

$$U_1^{(0)}(t,t_0) = 1. \quad (1.1.4b)$$

This expansion is termed as Feynman-Dyson expansion. The second term onwards correspond to first, second and so on ordered solutions of eq.(1.1.3). The power series in $H(t)$ converge more rapidly the closer $U(t,t_0)$ is to $U(t,t)$. The calculation of higher order expansions become increasingly complicated and so one is constrained to stop at the lower order approximations.
This conventional perturbation theory has certain practical disadvantages. For example any truncated expansion to the evolution operator is not unitary and this method is reliable only for small times and weak perturbations. Alternative expansions to the evolution operator which produce unitary approximations to \( V \) at the truncated levels are thus preferable.

1.1.2 Exponential Perturbation Theory:

Exponential form to the evolution operator is very convenient to define unitary approximations. Two such expansions which posit an exponential form to the evolution operator are the Magnus\(^8,9\) and Fer\(^9,16\) expansions. Of these two expansions Magnus expansion have been extensively applied.

In Magnus expansion\(^8,9\) \( U(t, t) \) is expanded as

\[
U_1(t, t_0) = \exp \left[ A(t, t_0) \right], \quad (1.1.5a)
\]

\[
A(t, t_0) = \sum_{n=1}^{\infty} \lambda^n A_n(t, t_0), \quad (1.1.5b)
\]

The operator \( A \) is chosen as anti-hermitian to produce unitary approximation to \( U \). In this expansion \( A \) is an infinite series in which the \( n \)th term is a sum of integrals of \text{n-fold} multiple commutators of \( H(t) \). For example, the first few terms in \( A \) are\(^9\)

\[
A_1(t, t_0) = -i \int_{t_0}^{t} dt' H(t'), \quad (1.1.5c)
\]
The Magnus expansion can be reduced to a simplified form when the hamiltonian is expressible in terms of the generators $G_i$ of a finite dimensional Lie algebra $L$.

\[
A_2(t,t_0) = \frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_2} dt_2 [H(t_1), H(t_2)], \tag{1.1.5d}
\]

In this case the exponent $A$ must also be a linear combination of the Lie elements,

\[
H_i = \sum_{i=1}^{n} h_i(t) G_i, \tag{1.1.6a}
\]

\[
[G_i, G_j] = \sum_{k} C_{ij}^k G_k; G_i, G_j, G_k \in L. \tag{1.1.6b}
\]

By applying closure property of the generators of Lie algebra and simplifying, the Magnus expansion reduces into a set of nonlinear differential equations in $A$. In the Fer expansion\textsuperscript{9,16} the evolution operator is written in the form

\[
U(t,t_0) = \exp(\lambda S_1)\exp(\lambda^2 S_2)\exp(\lambda^3 S_3)\ldots \tag{1.1.8}
\]

The recursive solutions to $S$ are obtained as in Magnus expansion.

There are several applications of Magnus expansion. Important among them are applications to NMR and optical spectroscopy.\textsuperscript{10} Scheck et al.\textsuperscript{11} and others applied this theory to high order molecular multi-photon excitation and noted that Magnus
expansion provides a practical method to go beyond the Rotating Wave Approximation (RWA). Cross\textsuperscript{12} has studied rotationally inelastic scattering using second order Magnus expansion with a classical correction to the inelastic part and the results are in good agreement with the accurate results.

Several authors have discussed the convergence of Magnus expansion.\textsuperscript{8,13} Pechukas and Light\textsuperscript{8,11} discussed about the convergence of Magnus expansion in the impulse limit. The first term in the Magnus expansion suffices provided the perturbation is infinitely brief and infinitely strong. Applications to harmonically driven two-level system, two level system in a rotating field and a multiple pulse model by Salzman\textsuperscript{13} showed that Magnus expansion in Schroedinger picture diverges. Several of the applications in interaction picture faced no divergence problems.\textsuperscript{13} The main drawbacks of the Magnus expansion are the equations for the generators A obtained from eg.(1.1.3) are infinite order polynomials. Under certain exotic conditions, the existence of the solution itself is doubtful.\textsuperscript{8(a),14}

1.1.3 Degenerate Perturbation Theory:

An inherent weakness of any perturbation expansion is that when two or more states interact strongly, the perturbation expansion either diverges or converge very slowly to be of any practical use. To deal with such situations quasi-degenerate perturbation theories have been developed. In these theories the interaction in the subspace M spanned by the strongly interacting states (called the model space) is treated exactly. The (weaker)
couplings between the model space and its complimentary virtual space are treated by perturbation theory. To this end a wave operator \( \Omega \) is defined such that

\[
\begin{align*}
UP &= \Omega U_k', \\
U_k &= PUP.
\end{align*}
\tag{1.1.9}
\tag{1.1.10}
\]

Thus

\[
\Omega = UP (PUP)^{-1}.
\tag{1.1.11}
\]

Here \( P \) is the projection operator onto the model space \( M \). The wave operator is now obtained from perturbation theory

\[
\Omega = 1 + \sum_{n=1} \lambda^n \Omega^{(n)}
\tag{1.1.12}
\]

and an effective hamiltonian \( H_{eff} \) is posited to generate the model space dynamics.

\[
i\hbar \dot{U}_k = H_{eff} U_k'.
\tag{1.1.12}
\]

Jolicard and co workers discussed an iterative scheme to calculate \( \psi \) and \( H_{eff} \) in a self consistent manner. Jolicard\(^{18}\) used this approach to follow the dynamics of a triatomic molecule in intense monochromatic fields and found that the method is dependable.

Another perturbation approach which is used in the study of dynamical evolution is the Generalized Van Vleck (GVV) perturbation theory.\(^{19}\) It is generally used along with the Many Mode Floquet theory (MMFT)\(^{(e),(f)}\). MMFT converts an
N-level time-dependent system exposed to polychromatic fields into an infinite dimensional time-independent eigenvalue problem. GVV perturbation theory is then used to Block diagonalise this time-independent Hamiltonian\(^{19,q}\) such that the coupling between the model space and the remainder of the configuration space is reduced to a desired order. The model space Hamiltonian can then be considered as a total effective Hamiltonian to approximately solve a set of nearly degenerate states. GW perturbation method can also be used along with the Floquet Liouville Super Matrix (FLSM) approach for determining the quantum dynamics.

1.1.4. Perturbation theory in dynamical basis sets:

The studies described above use eigenfunctions of some suitably chosen operator (the unperturbed Hamiltonian) as the basis of the Hilbert space. The convergence of the perturbation theory depends critically on the choice of the basis set. Several authors have considered the use of dynamical basis functions to represent the Hilbert space in recent years. These functions change in time and are tailored to follow (to the extent possible) the exact wave packet in time. The details of the construction of such dynamical basis functions is discussed later in the context of the variational approaches.

Recamier et al.\(^{20}\) described the time evolution of linearly driven parametric oscillators using an operator algebra. They make use of a dynamical basis set expansion and the vibration-vibration coupling is treated perturbatively.

In recent years another method which employs
perturbative treatment is the Perturbation Corrected Time-Dependent Self-Consistent Field (PCTDSCF) method. This method when applied to He + H₂ vibrationally inelastic collisions produced results in good agreement with the exact results.

1.2. VARIATIONAL APPROACHES

In the variational approaches, the wave packet is expanded in terms of a set of basis functions

\[ \psi = \sum_n c_n(t) \chi_n. \]  

(1.2.1)

The coefficients \( c_n \) are obtained from the Frenkel variational principle and satisfy

\[ i\dot{c}_n = (H - H_0)c_n, \]  

(1.2.2a)

\[ i\dot{\chi}_n = H_0\chi_n. \]  

(1.2.2b)

One can carry out the expansion in eq. (1.2.1) in terms of either stationary basis functions whose probability distribution remains constant in time

\[ d/dt(\chi_n^* \chi_n) = 0 \]  

(1.2.3)

or in terms of dynamical basis functions where eq.(1.2.3) does not hold. The major questions to be addressed in this approach are regarding the representation to be used for the basis vectors and the time propagation. These are discussed below.
1.2.1. Stationary Basis Set Methods:

In these methods the expansion functions $x$ are assumed to be either the solutions of time-independent Hamiltonian or some functions which do not vary with time. One of the general approaches for the construction of basis is the variational matrix representation method. In this $x$ are expanded in terms of an orthonormal basis of $N$ functions and the variational coefficients are determined by diagonalisation. The effort in this Variational Basis Representation (VBR) depends on the complexity of the Hamiltonian matrix evaluation and the size of the matrix representation required for adequate accuracy. In general the size of the matrix is large demanding high computational effort even for slightly larger systems.

Light and co-workers suggested a different representation known as Discrete Variable Representation (DVR). In this representation the approximate solutions are expressed at a well defined set of coordinate points in a grid space:

$$x_n(q) = \sum a_n g_n(q), \quad (1.2.4)$$

where $g_n(q)$ are chosen from an orthogonal basis. One way is to use Gaussian Quadrature points of orthogonal polynomials:

$$g_n(q) = w_\alpha(q) p_n(q), \quad (1.2.5)$$

where $q$ are quadrature points, $w_\alpha(q)$ is a weight function and $p_n(q)$ is an orthogonal polynomial. The orthogonality and
completeness relations are given by

\[ \sum_{\alpha=1}^{N} g_{\alpha}(q_{\alpha})w_{\alpha}(q)g_{j}(q_{\alpha}) = \delta_{ij}, \]  

(1.2.6a)

\[ \sum_{k=1}^{N} q_{k}(q_{\alpha})w_{\alpha}w_{\beta}^{1/2}g_{k}(q_{\beta}) = \delta_{\alpha\beta}. \]  

(1.2.6b)

A special case of orthogonal representation is the Fourier method. In this representation the orthogonal functions \( g_{k}(q) \) are chosen as

\[ g_{k}(q) = \frac{1}{\sqrt{L}} \exp(i2\pi kq/L), \]  

(1.2.7a)

where

\[ k = -(N/2 - 1), \ldots 0 \ldots N/2, \]  

(1.2.7b)

also the sampling points are considered to be equally spaced

\[ q_{i} = (i-1)dq \]  

(1.2.7c)

and \( L \) is the length of a conveniently chosen box. The choice of \( g(q) \) in eq.(1.2.6) indicates the periodic boundary conditions. This representation in conjunction with the Fast Fourier Transform (FFT) algorithm scales the numerical effort semi-linearly with the phase space volume. This is the main attraction with the Fourier method representation.

The next step to representation of the wave function is the representation of operators. The result of hamiltonian operation on the wave function is the key step for determining the time evolution. Usually the hamiltonian is considered as the sum
of potential and kinetic energy operators.

\[ H = T + V. \] (1.2.8)

As the potential energy operator \( V \) is local in coordinate space, its operation is just a multiplication. But the kinetic energy operator \( T \) is not local in coordinate space. One way to perform kinetic energy operation on the function \( x \) is to transform it to momentum space by FFT, multiplying by \( T \) and then transform it back to coordinate space by inverse FFT. Another way is to apply Finite-Difference (FD) method. By invoking FD representation to \( T \), operation of \( T \) on \( x \) gives up to second order,

\[ T_{FD} x_n = -\hbar^2 (\chi_{n+1} + \chi_{n-1} - 2\chi_n) / 2m \sigma_n^2. \] (1.2.9)

More general expressions for infinite order FD have also been given. Even if the \( T \) operator is represented in other coordinate representations like spherical coordinates, the local representation is possible for the radial part of the operator by using the Bessel transform. But changing the angular parts into local representation is very complicated.

Before time propagation one has to set the initial conditions. The choice is specific for a specific problem. For bound degrees of freedom usually an eigenstate of the unperturbed hamiltonian is set equal to the initial condition. For the translational degree of freedom gaussian wave packet form is the common choice.

Mowrey et al. in studying the scattering problems used a method, which they termed as Close Coupling Wave Packet (CCWP)
method. In this method to describe the translation motion they use wave packet evolution by means of Chebychev expansion and rotational motion using time-independent coupled Channel methods. The computational effort required for CCWP method is more than that for Coupled Channel methods but the results are accurate at least for the scattering problems.

An approach which converts time-dependent periodic hamiltonians into time-independent hamiltonians is the Floquet theorem. If the hamiltonian is periodic, i.e. $H(t+T) = H(t)$, according to Floquet theorem there exists a set of Floquet modes which are particular solutions of the Schroedinger equation with unique behaviour that the density matrices are periodic. The time evolution operator $U(t+T)$ is unitary and so in the determination of its eigenstates no spurious effects are encountered. Floquet method have been generalized to apply for the nonperiodic hamiltonians also when the system is considered in the polychromatic fields.

One generalization of the Floquet method is the Quasivibrational Energy (QVE) formalism which give quasivibrational energies. These are useful in determining the rates of multi-photon dissociation process. Another method which provide a tool for determining the QVEs is the Complex Scaling Fourier Grid hamiltonian (CSFGH) method developed by Chu.

1.2.2. Dynamical Basis Set Methods:

In these methods the basis functions $\chi_n$ follow the wave packet $\psi$ moves through space.
The functions $x$ are taken to be the solutions of some reference time-dependent Schrödinger equation

$$i\dot{\chi}_n = H_0(t)\chi_n.$$ \hspace{1cm} (1.2.11)

Assuming that $\chi_n$ remain orthogonal throughout their evolution the $C$-coefficients are given by

$$i\dot{C}_n = \sum_n <\chi_n|H-H_0|\chi_m>C_n.$$ \hspace{1cm} (1.2.12)

The basic premise in the use of dynamical basis sets is that if $H$ is judiciously chosen such that $H-H$ is small then the expansion (1.2.1) requires very few terms for convergence. This feature is very advantageous when wave packet travels long distances especially for many body systems.

The important methods which provide dynamic representation are the Gaussian Wave Packet (GWP) methods, time dependent self consistent field (TDSCF) method and the Lie-algebraic methods. In the following sections we discuss these methods.

1.2.2a. Gaussian Wave packet Propagation methods: \textsuperscript{31}

GWP methods are developed and extensively applied by Heller.\textsuperscript{31,32} The main feature of GWP is that the wave function is parameterized as a complex traveling gaussian of the form

$$\psi(q,t) = \sum_{j=1}^{\infty} C_j(t) \chi_j(q,t).$$ \hspace{1cm} (1.2.10)
\[ \psi(q,t) = \exp\left[\frac{i}{\hbar}(a_t(q-q_t)^2 + p_t(q-q_t) + \gamma_t)\right], \quad (1.2.24) \]

where \( q_t, p_t \) are the expectation values of the position and momentum. \( a \) is the width parameter and \( \gamma \) is the phase of the wave packet. The potential in the Hamiltonian is expanded as a Taylor's series around \( q \) and terms beyond second order are neglected. This is known as Locally Harmonic Approximation (LHA). Substituting \( \psi(q,t) \) in TDSE and comparing the coefficients of like powers of \( q-q \) gives the equations of motion

\[ \dot{q}_t = \frac{p_t}{m}, \quad (1.2.14) \]
\[ \dot{p}_t = -\left(\frac{\partial V}{\partial q}\right)_{q=q_t}, \quad (1.2.15) \]
\[ \dot{a}_t = -2a_t/m - 1/2\left(\frac{\partial^2 V}{\partial q^2}\right)_{q=q_t}, \quad (1.2.16) \]
\[ \dot{\gamma}_t = i\hbar a_t/m + p_t q_t - \frac{p_t}{m} - V_0. \quad (1.2.17) \]

The eq. (1.2.14), eq.(1.2.15) are the classical Hamilton equations of motion for the system concerned and hence Heller referred this method as semiclassical GWP method. This method is exact only for harmonic potentials. It becomes an approximation for anharmonic potentials as the wave packet form does not remain as gaussian during propagation for these potentials. This method is also known as Thawed Gaussian Approximation (TGA).

Heller suggested an approximation over GWP which reduces the computational effort considerably. This is obtained by freezing the widths of the wave packet during the propagation and
is known as Frozen Gaussian Approximation (FGA).

Coalson and Karplus\textsuperscript{34} and Lee and Heller\textsuperscript{31} extended this method to obtain formally exact solution for multi-dimensional quantum mechanical problems involving anharmonic potentials. They invoke a time-dependent basis set of travelling harmonic oscillator eigenfunctions, with the width parameter controlled by local hessian as in GWP. The potential energy is expanded in Taylor's series and terms up to nth order are retained. The wave function is parameterized as

$$\psi(q,t) = f(q,t) \exp[g(q,t)]. \tag{1.2.18}$$

The gaussian form is assumed for $\exp[(g(q,t)]$. The functions $f(q,t)$ are expanded as

$$f(q,t) = \sum C_n(t) \phi_n(q,t) = \sum C_n(t) a_n H_n[k_t(q-q_t)], \tag{1.2.19}$$

where $n$ is the nth order Hermite Polynomial $H_n$ and $a_n$ and $k_t$ are the normalization constant and width parameter. Substituting the eqs. (1.2.18) and (1.2.19) in TDSE results in the equations of motion for the parameters $q_t, p_t, \alpha_t$ and $\gamma_t$.

Another extension to GWP is the Generalized Gaussian Wave Packet Dynamics (GGWPD).\textsuperscript{35} This method is an extension of GWP into complex phase space retaining time as real. This method does not restrict wave packet to be gaussian throughout the propagation unlike GWP. Moreover classically forbidden regions can be explored using GGWPD. By using the symmetrized
trajectories the norm is conserved even for a superposition of gaussians. The accuracy of the results are improved over GWP.

GWP has been extensively used in determining variety of dynamics\(^{36}\) such as scattering, photodissociation process, etc. The qualitative description is good in all the applications. In the application of GWP in conjunction with time-dependent variational principle even quantitative accuracy was obtained for some applications.

The errors in these semiclassical GWP methods increase faster than linearly with time and so the semiclassical description may not be adequate for the systems which require the wave packet to travel longer distances. To avoid such situations Huber and Heller proposed Hybrid mechanics.\(^{39}\) In this method the semiclassical description is used to construct the quantum mechanical time propagator for a finite time step, then using this propagator the evolution of the system is determined quantum mechanically for longer times.

1.2.2b. Time-Dependent Self-Consistent Field Methods:\(^{40,60}\)

TDSCF method is often referred as Time-Dependent Hartree (TDH) method. The computational effort scales linearly with number of modes in the system and so even the many mode system dynamics can be attempted to study using this method. It has been suggested\(^{40}\) in the early days of quantum mechanics itself but its exploration appeared much latter. The early applications\(^{41}\) were to study the excitation spectra of multi-electron systems, dynamics of nuclear reactions such as fission, fragmentation and compound nucleus formation etc.. Heller\(^{42}\) discussed TDSCF in
the context of time dependent variational principle. Harris discussed first in the context of vibrational spectroscopy. Quite a number of studies on TDSCF appeared in recent years.

Each mode in the system is formally separated in the TDSCF method and is governed by time-dependent average potential which is obtained by averaging the full potential over all the other modes. To this end the wave function is expanded as a single Hartree product of each mode function

$$\psi(q_1, q_2 \ldots q_n, t) = \prod_{i=1}^{N} \phi_i(q_i, t), \quad (1.2.20)$$

where \( N \) is the number of degrees of freedom in the system concerned. Writing hamiltonian for the system in simple form

$$H = \sum_i T_i + V(q_1, q_2 \ldots q_n), \quad (1.2.21)$$

with \( T_i \), the kinetic energy of the ith mode and \( V \) is the potential energy. By invoking the variational principle \( \langle \delta \psi \mid H - \text{id}/dt \mid \psi \rangle = 0 \), the SCF equations are obtained as

$$i\hbar \frac{d\phi_i(q_i, t)}{dt} = h_1^{\text{SCF}}(q_i, t) \phi_i(q_i, t). \quad (1.2.22)$$

The TDSCF ith mode hamiltonian is

$$h_1^{\text{SCF}}(q_i, t) = h_i(q_i) + \bar{V}_i(q_i, t), \quad (1.2.23)$$

where

$$h_i(q_i) = T_i + V_i(q_i) \quad (1.2.24)$$

and
The single-mode description of TDSCF is represented by eq. (1.2.23) with each mode having its own Hamiltonian. Here the time evolution of the system is governed by the time-dependent SCF potential (eq. (1.2.25)) and the evolution of the $i$th mode depends indirectly on the other modes through this average potential.

The TDSCF method conserves the total energy of the system, i.e.

$$\frac{a}{dt} \langle \psi | H | \psi \rangle = 0.$$  (1.2.26)

This property is important for energy transfer studies. The norm of the wave function is also conserved in this formulation as the hermiticity of the Hamiltonian is not affected.

From studies of nuclear dynamics it was found that TDSCF suffer from spurious state problem due to the restrictions imposed on the wave packet. Methods have proposed to eliminate this problem.\textsuperscript{41} Average properties such as dissociation lifetimes, single-mode energy distribution are predicted well, whereas correlation between states or state to state transition probabilities are badly reproduced by TDSCF as expected.

Gerber et al.\textsuperscript{43} developed different versions of TDSCF. In the fully quantum mechanical version of the method the functions $\phi(q,t)$ are expanded in terms of eigenstates $u_i(q)$ of the bare mode Hamiltonian $h_i(q_i)$. 

\begin{equation}
\overline{v}_i(q_i,t) = \sum_j \langle \phi_j | v_{ij}(q_i,q_j) + \ldots | \phi_i \rangle.
\end{equation}  (1.2.25)
where energies $c^l_v$ are eigenvalues of $h(q)$ and $C_v$ are unknown coefficients. Substitution of eq. (1.2.27) in the TDSE results in the standard set of coupled first order differential equations for $C$. The TDSCF potentials then appear in the form

$$\phi_i(q_i, t) = \sum C_{i\nu}(t) u_{\nu}(q_i) \exp[-ic^l_{\nu}(t)], \quad (1.2.27)$$

Buch et al.\textsuperscript{44} have explored the utility of the classical limit of TDSCF. In the self-consistent trajectory bundles approach the average potential may be written in terms of trajectories:

$$\overline{v}_i(q_i, t) = \sum_{v} \left( \sum_{j v} c_{j l v}^* c_{l w} \langle u^l_j | v_{ij}(q_i, q_j) | u^l_w \rangle \right) \times \exp[-it(c^l_v - c^l_w)/\hbar]. \quad (1.2.28)$$

The $q^{(\lambda)}(t)$ trajectory is calculated from TDSCF nth mode hamiltonian labelled by $A$ and $N_t$ is the number of trajectories employed. The trajectory equations for the $q(t)$ in correspondence with single-mode TDSCF Schroedinger equation (eq.1.2.22) appear as

$$\dot{q}_i(t) = \left( \frac{\partial h^{SCF}_i}{\partial p_i} \right), \quad (1.2.30)$$

$$\dot{p}_i(t) = - \left[ \frac{\partial h^{SCF}_i}{\partial q_i(t)} \right]. \quad (1.2.31)$$
Here $h^{\text{SCF}}$ is classical analog of eq. (1.2.23). In this scheme $N \cdot N_t$ equations are needed to solve the system.

Application of TDSCF in the classical limit to dissociation dynamics of several van der Waals complexes by Buch et al.** showed that it works well for both weak and strong coupling dissociation dynamics in semi-quantitative way in accordance with the experimental and quantum mechanical results.

The convergence of the results of TDSCF method depends on the choice of the coordinates. This generally done by physical intuition or by looking for the natural separability of the modes. It is proved that the optimized coordinates produce better results. The main draw back of the TDSCF is that important correlations between various modes are left out, which describe many important chemical processes. Hence TDSCF fails in determining the long time dynamics, i.e. when the correlations become significant. Attempts have made to correct for these correlations at the same time retaining the simplicity of the mean-field description.

The Time-Dependent Rotated Hartree (TDRH) method developed by Cederbaum et al.\textsuperscript{54,55} is one of the extended versions of TDSCF method. In this method inclusion of time-dependent unitary operators acting on the Hartree product made possible the description of correlations between various degrees of freedom to a limited form. In this approximation the exact wave function is written as

$$\psi_j(t) = \prod_{k=1}^{N} U_k \phi_j(t), \quad (1.2.32)$$

where
\[ U_k = \exp(i\alpha_k A_k). \] (1.2.33)

\( U_k \) is considered as unitary and so \( \alpha \) are real parameters and \( A_k \) are hermitian operators. The operator \( U \) is chosen such that it involve all possible operators which cause the mixing of different degrees of freedom. This made possible the inclusion of correlations to certain extent. The ansatz (1.2.32) is termed as TDRH wave function as \( U_k \) describe the generalized rotations.

By employing Lagrange variational principle on TDSE, the equation to be solved is\(^{37}\)

\[ \text{Re} \left< \delta \psi \right| \frac{i\partial}{\partial t} - H \left| \psi \right> = 0, \] (1.2.34)

or by employing McLachlan variation principle\(^ {37}\)

\[ \text{Im} \left< \delta \psi \right| \frac{i\partial}{\partial t} - H \left| \psi \right> = 0. \] (1.2.35)

Substitution of eq.(1.2.32) and eq.(1.2.33) in these equations yield the equations for \( \phi \) and \( \alpha_k \). The SCF equations for \( \phi \) obtained by both the variational principles are the same but for the parameters they are different.

The application of the approach to a model coupled oscillators\(^ {54,55}\) showed better converged results than TDSCF method. The computational effort involved in TDRH is slightly more than that involved in TDSCF method but when compared to basis set calculation it is very low.

To account for the important correlations one can add configurations to TDSCF as suggested by Makri and Miller\(^ {56}\) which
is termed as Multi-Configuration Time-Dependent Self-consistent field (MCTDSCF) method. This description allow more flexibility in the wave function which makes it possible to incorporate of the important correlations. Latter on Meyer et al.\textsuperscript{57} derived relatively simple equations for n degree of freedom system with m configurations. They write the approximate time-dependent multi-configuration trial wave function in the form

$$\psi(q_1, q_2, \ldots, q_n) = \sum_{j_1=1}^{m_1} a_{j_1}^{(1)}(t) \phi_{j_1}^{(1)}(q_1, t), \ldots, \sum_{j_n=1}^{m_n} a_{j_n}^{(n)}(t) \phi_{j_n}^{(n)}(q_n, t),$$

(1.2.36)

where m are the number of single particle functions which build up the respective modes, n is the number of modes in the system. To eliminate the redundant configurations the condition $m \leq n \prod_{i=1}^{n} D_i$ is imposed. The single particle functions are assumed to be orthogonal at any time:

$$\langle \phi_{j}^{(k)} | \phi_{j}^{(k)} \rangle = \delta_{jj},$$

(1.2.37)

The appearance of redundant configurations also require the condition

$$\langle \phi_{j}^{(k)} | \phi_{j}^{(k)} \rangle = 0.$$  

(1.2.38)

(k)  

Defining the matrices $A$ and $\phi$ to make the equations look simpler

$$A_j^{(k)} = a_{j_1}, \ldots, j_{k-1}', j_{k+1}', j_n'.$$  

(1.2.39)
invoking the Dirac-Frenkel variation principle and the conditions eq. (1.2.37) and eq. (1.2.38) the working equations look as

\[ \dot{\phi}_{j_1 \ldots j_n} = \langle \phi_{j_1}^{(1)} \cdots \phi_{j_n}^{(n)} | H | \psi \rangle, \]

\[ i \phi = \sum \left( A^{(k)} + (k) \right)^{-1} \left[ \langle \phi_{j_1}^{(k)} | H | \psi \rangle - i \sum \Lambda_{j_1}^{(k)} \phi_{j_1}^{(k)} \right]. \]

The application of MCTDSCF to a model coupled oscillators by Meyer et al. and other applications\textsuperscript{57,58} showed good convergence.

Another version to MCTDSCF is TDHG-CI\textsuperscript{59}. The strategies in the two theories are similar but they differ in detail. In MCTDSCF each basis function in each coordinate for every mode is individually optimized self-consistently with the evolution of superposition coefficients. In TDHG-CI, using McLachlan Variation, a global effective potential is constructed to guide all the travelling basis functions. Once the basis set is constructed, the configuration interaction phase is carried out in the complete basis. Application of this strategy to collinear inelastic atom-Morse oscillator scattering\textsuperscript{59} showed that it works well for obtaining the dynamics of many body quantum systems.

In a very recent article Vekhtar et al.\textsuperscript{60} suggested TDSCF2-CI approach which has the advantages of Pair correlations and of configuration interaction. They write \( \psi \) as

\[ \psi_{\alpha\beta}(TDSCF2) = \psi_{\alpha\beta}(\alpha, \beta, t) \prod_{i, \alpha, \beta} \psi_i(i, t), \]
where \((\alpha, \beta)\) is a mode pair whose interaction has to be exactly treated. The equations for other modes are the same as in the TDSCF method. But the potential for these methods looks as

\[
v_{\text{eff}}^{\alpha\beta} = V(\alpha, \beta, t) + \sum_{i} V_{\alpha\beta}(i, t). \tag{1.2.44}
\]

The correlated pair is chosen differently in each of the \(N(N-1)/2\) configurations.

1.2.2c. The Lie-Algebraic construction of dynamical basis:

Micha and co workers have applied the Lie algebraic method to study the atom - diatom and diatom - diatom collisions. They expand the interaction potential in Taylor series and truncate at quadratic level so that the finite dimensional quadratic Lie algebra can be used to construct a reference evolution operator to propagate the dynamical basis functions. The elements \(q^2, qp+pq, p^2, q, p\) in this order are contained in the Lie algebraic structure. The interaction picture hamiltonian is then written in terms of the elements of the algebra, \(X\) which are closed under commutation:

\[
H_i(t) = \sum_k f_k(t) X_k. \tag{1.2.54}
\]

The reference evolution operator is then constructed as

\[
U_i(t, t_0) = \prod_{n=1}^{s} \exp[-i\alpha_n(t)X_n]. \tag{1.2.55}
\]

26
Substituting $U$ and $H$ in TDSE and using Hausdorff expansion results in the governing equations for $a(t)$. In the case of

**diatom-diatom** collisions, part of the interaction potential is not closed under commutation and so the algebra becomes slightly complicated. To solve this residual coupling they use the perturbation theory.

Benjamin\textsuperscript{62} formulated a semiclassical algebraic theory in which the vibrational motion is described quantum mechanically using an appropriate algebra and the translational motion is described by classical equations of motion. For the Lie-algebraic structure when the full quadratic algebra is used he termed the method as **Quadratically Driven Parametric Oscillator** (QDPO) method. In a different approximation the quadratic terms are neglected and the method is termed the Linearly Driven Parametric Oscillator (LDPO) method. In another approximation a canonical transformation is performed such that it eliminates the effect of quadratic elements and the approach is termed as **Quadratically Driven Scaled oscillator** (QDSO). Application was made to atom - diatom and diatom - diatom collisions and the values are in good agreement with exact quantum mechanical results and the computational effort is comparatively low.

The role of time varying frequency in the vibrational transition of a nonlinearly driven oscillator is studied by Shin\textsuperscript{63} using Lie algebraic method. The Lie algebraic structure contains the set \{ $a^+a^+, a^+, a$, $a$ \}. The transition probabilities are computed over wide range of collision energies to study the effect of time-dependent frequency.

Gilmore and Yuan\textsuperscript{64} have studied vibrational
translational interaction and computed the scattering matrix elements using this approach. They use group theoretic root space diagram to construct the evolution operator, the double photon algebra which is the sub algebra of C representation was used. The evolution operator in terms of $a$ and $a^\dagger$ is then looks as

$$U(t) = \exp(ra^\dagger + Ra^2) \exp(\eta (n+1/2)+\delta I) \exp(la + la^2),$$ (1.2.56)

where $r, R, \eta, \delta, l, L$ are time-dependent functions. The convergence of the transition probabilities encouraged the extension of the method to complicated systems.

Shi and Rabitz studied a parametric amplifier and collinear collision of an atom with a Morse oscillator using a variational Lie algebraic formalism. In the study of parametric amplifier the algebraic set \{a^+_1a_1, a^+_2a_2, a_1a_2, a^+_1a_2, a^+_2a_1, a_1, a_2, a^+_1, a^+_2\} was used to construct the evolution operator. In the relatively complicated system of collinear collision of an atom with Morse oscillator only the relative motion was treated semiclassically using the Lie-algebraic method. The Morse oscillator part of the hamiltonian was solved by basis set expansion in Morse basis.

Kucar and Meyer solve TDSE using the dynamical basis set. In determining the time dependence of the basis set they utilize the Lie-algebraic structure to construct the evolution operator. The time-dependent basis \(\chi(q,t)\) is defined as

$$\chi_n(q,t) = U(t) \phi_n(x) = \prod_{k=1}^m \exp[i\alpha_k(t)A_k],$$ (1.2.57)
where \( \alpha_k \) represents a real parameter and the generator \( A_k \) is a hermitian operator. The wave function \( \psi(q, t) \) is then expanded in this basis as

\[
\psi(q, t) = \sum_n a_n(t) \kappa_n(q, t),
\]

\[
= U(t) \phi(q, t). \tag{1.2.58}
\]

Keeping in view that the generators \( A_k \) form a Lie algebra, the evolution operator is constructed as

\[
U(t) = \exp(-iqp) \exp(ipq) \exp(i\beta q^2) \exp(i a_t (qp+pq)) \exp(i \gamma H_0) \exp(i \delta t), \tag{1.2.59}
\]

where the operator set \( \{1, q, p, q^2, (qp+pq), H\} \) forms a Lie algebra. The working equations are derived for a multi-dimensional system. The system is well represented in the time-dependent basis but the problem is that the differential equations to be solved may become stiff in the course of the time propagation.

Echave et al.\textsuperscript{67} have applied the Lie-algebraic theory to build the interaction potential in the intermediate picture and used it to calculate the physical observables. They write the TDSE in terms of \( H \) and \( U \) as

\[
\text{i} \hbar \frac{dU_{\text{eff}}(t, t_0)}{dt} = H_{\text{eff}} U_{\text{eff}}(t, t_0), \tag{1.2.60}
\]

where

\[
U_{\text{eff}}(t_0, t_0) = 1.0. \tag{1.2.61}
\]
The wave function is then represented as

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

They write the equation for the \( \phi(t) \) as

\[ \text{i} \hbar \frac{d\phi(t)}{dt} = H_{\text{i}} \phi(t), \]

\[ \phi(t_0) = \psi(t_0), \]

where \( H \) is defined in terms of \( H \) and \( U \)

\[ H_{\text{i}} = U_{\text{eff}} (H - H_{\text{eff}}) U_{\text{eff}}. \]

\( H \) is expanded as

\[ H_{\text{eff}} = \sum_{i=1}^{n} h_{i} x_i, \]

where \( \{x_1, x_2, \ldots, x_n\} \) is a set of hermitian operators. The formation of \( H \) matrix is facilitated by defining

\[ x_j'(t) = \sum_{k=1}^{n} G_{jk}(t) x_k. \]

The time-dependent matrix elements \( G \) satisfy linear equations of motion. Another matrix \( F \) is defined such that

\[ [x_j', H_{\text{eff}}] = \sum_{k=1}^{n} F_{jk} x_k. \]
The matrix $G$ satisfy the equation

$$i\hbar \frac{dG}{dt} = FG, \quad G(t_0) = 1.0.$$ (1.2.68)

The working equations are eq.(1.2.63), (1.2.64) and eq.(1.2.68). An application was made to study the VT transfer in He – $H_2$ collisions.

An application of algebraic theory to determine the photodissociation dynamics of CH I was made by Someda et al.\textsuperscript{68} They define the evolution operator as

$$U(t) = \prod_{1=1}^{n} \exp [i\eta_i(t) X_i],$$ (1.2.69)

where $\{X, X, ...X\}$ form a Lie algebra. The coefficients $\eta$ are determined by employing Dirac–Frenkel time-dependent variational principle.

Recently Lin et al.\textsuperscript{69} analyzed the molecule-surface collisions of $^4$He and $^3$He on the (001) face of LiF crystal using Lie-algebraic method. They have used the six dimensional algebra which contains the elements $I, a, a, aa, a, a$ to construct the evolution operator.

1.2.3 Integration Schemes:

The propagation of wave function in time requires the construction of evolution operator. The formal solution to $U$ in eq.(1.0.4) is

$$U = \exp(-i\mathcal{H}t/\hbar).$$ (1.2.70)
The construction of evolution operator in this way is generally impossible as the exponentiation of the Hamiltonian is a complicated job. To simplify the construction of evolution operator one can expand the above expression in Taylor's series and truncate the expansion after few terms. The simplest is to write

\[ U = 1 - i\hbar dt/\hbar. \] (1.2.71)

This approximation to the evolution operator in conjunction with finite difference formula for the second derivative of the coordinate in the kinetic energy operator provide an explicit integration scheme. This scheme is known as the crude Euler method. This explicit scheme is known to be unstable as it does not conserve the time reversal symmetry of the Schroedinger equation.

McCullough and Wyatt used Crank-Nicholson approximation to the evolution operator. In this approach U is approximated as

\[ U = [1 + i\hbar dt/2\hbar]^{-1} [1 - i\hbar dt/2\hbar]. \] (1.2.72)

This approximation provides an implicit integration scheme along with finite difference formula for kinetic energy operator. In implicit integration scheme a system of equations need to be solved. While stable it requires high computational effort because it involves inversion of matrices.

A stable integration scheme was developed by Askar and
Cakmak\textsuperscript{71} in which they use the symmetric relation

$$\psi(t+dt) - \psi(t-dt) - [\exp(-iHdt/h) - \exp(iHdt/h)] \psi(t). \quad (1.2.73)$$

Expanding the above two exponential terms in Taylor's series and truncating it after two terms results in the explicit second order differencing propagation scheme

$$\psi(t+dt) = \psi(t-dt) - (2iHdt/h) \psi(t). \quad (1.2.74)$$

This scheme preserves norm and energy if the hamiltonian operator is hermitian. This energy and norm conservation accumulates error in the phase. This becomes significant after certain steps of time propagation.\textsuperscript{5} This is the propagation scheme used in many applications of the finite difference and Fourier methods.\textsuperscript{72} Formulae for higher order schemes were discussed by Manthe and Koppel.\textsuperscript{73}

Fiet and Fleck developed a split time propagation scheme.\textsuperscript{7*} In this the evolution operator in eq. (1.2.70) is split into two operators in which one consists of potential energy operator and the other kinetic energy operator. These two operators propagate the wave function separately.

$$\exp(-iHdt/h) \approx \exp(-iTdt/2h) \exp(-iVdt/h) \times \exp(-iTdt/2h). \quad (1.2.75)$$

This method is used generally in conjunction with FFT. In this method norm is conserved as each split time evolution operator is
unitary, but error accumulates due to non commutability of kinetic and potential energy operators.

In these short time propagation schemes error accumulation is inevitable somewhere in the time propagation. For the time-independent hamiltonians one can define a global propagator in which a polynomial expansion is used for the evolution operator.

\[ U(t) = \sum_{n=0}^{N} a_n \phi_n (-iHt/h). \quad (1.2.76) \]

Here \( \phi \) are elements of some orthogonal polynomial set. Chebychev and Lanczos schemes have been shown to provide good expansions for these global propagator schemes. In the Chebychev scheme\(^{23,1} \) \( \phi_n \) are the complex Chebychev polynomials. The determination of propagated wave function in this scheme requires the operation \( \phi_n (-iH) \), which can be calculated using the Chebychev recursion formula,

\[ \phi_{n+1} = -2iH \phi_n + \phi_{n-1}. \]

The error accumulation is minimal in this scheme and it is uniformly distributed on all the eigenvalues and so the Chebychev polynomial expansion is optimal for the global propagators.

In the Lanczos scheme\(^{75} \) the recurrence relation for \( \phi_n(-iH) \) is

\[ \beta_j \phi_{j+1} = [H - \alpha_j] \phi_j - \beta_{j-1} \phi_{j-1}, \quad (1.2.78) \]

where
\[ \alpha_j = \langle \phi_j | H | \phi_j \rangle. \]  \hfill (1.2.79)

(3 is obtained from the normalization condition

\[ \langle \phi_{j+1} | \phi_{j+1} \rangle = 1. \]  \hfill (1.2.80)

The error accumulation is not uniform in this scheme and hence requires the stabilization procedures.\(^5\)

These two schemes are independent of the representation of the wave function. In these global evolution methods no intermediate results are obtained. One can split the propagation into smaller intervals in order to get the intermediate values but large increase in the number of intervals make the approach inefficient. In many applications, Chebychev ' and Lanczos recurrence schemes have been used for time propagation.

To deal with \textit{N}-level systems a simple computational technique called as \textit{time-slicer} has been suggested by Hirschfelder et al.\(^{37}\) In this procedure the time-dependent \textit{hamiltonian} is approximated by a sequence of time-independent \textit{hamiltonians}. At \(n\)th period \(H(t)\) is approximated by a constant hamiltonian (for a very small time period) \(H^{(n)}\), which can be written as

\[ H^{(n)} = H[(t_n + t_{n-1})/2]. \]  \hfill (1.2.81)

Since this technique does not require hamiltonian to be hermitian the effects of natural \textit{lifetimes} and the other relaxation parameters which we generally encounter in Electron Spin Resonance (ESR) and Nuclear Magnetic Resonance (NMR) applications can be
determined. The **time-slicer method** is a simple and efficient numerical procedure for the solution of both linear and nonlinear sets of coupled first and second order differential equations.

1.3. **NON-PERTUBATIVE APPROACHES**

In this section we discuss three non-pertubative and non-variational methods: the construction of the evolution operator by Lie-algebraic methods, the time-dependent coupled cluster method (TDCCM) and by the path integral approach.

1.3.1. Lie-algebraic construction of $U$:

As noted earlier, the Lie-algebraic methods have been mostly used to define **dynamical** basis set representation. However they can be used to construct the exact time evolution operator also. The algebraic approaches are developed on the realization that when the hamiltonian is an element of a Lie algebra, then the time evolution operator can be written as an exponential of a general linear combination of the elements of the algebra. The hamiltonian is expressible as

$$H = \sum_n h_n A_n,$$

(1.3.1)

where all the operators $A_n$ belong to the set $L$ that is closed under commutation

$$[A_n, A_m] = \sum_k C_{nm}^k A_k; A_n, A_m, A_k \in L, \forall n, m, k$$

(1.3.2)
The time evolution operator can then be written as an exponential of a general linear combination of all the operators of the algebra,\(^9\) i.e.

\[ U(t) = \exp \left[ \sum_n a_n A_n \right], \]  

(1.3.3)

alternatively in the Wei-Norman product form as

\[ U(t) = \prod_n \exp \left[ a_n A_n \right]. \]  

(1.3.4)

The variables \( a \) are time-dependent coefficients of the generators of the evolution operator. The governing equations for these coefficients are obtained by appealing to the TDSE (eq.(1.0.4)). One can chose perturbative Magnus expansion\(^8\) method or any nonperturbative approach\(^80\) to construct the evolution operator.

The algebraic approach is practical particularly when the concerned Lie algebra is finite dimensional. In that case the number of variables required to define the evolution operator are finite even if the system is considered in an infinite dimensional Hilbert space. Harmonic oscillator algebra is a finite dimensional algebra and is commonly used in the construction of the evolution operator for the quadratic hamiltonians which are elements of this algebra. Projection operator algebra is another algebra which is finite dimensional. The solution for the coefficients \( a \) is not trivial if the algebra is not semisimple.

A subset \( S \) of a Lie algebra \( L \) is called a subalgebra if it is closed under commutation, addition and multiplication by a scalar. A subalgebra \( S \) is called an ideal if all the commutators \([X, Y]\) of
X ∈ S and Y ∈ L is in S. The union of all the solvable ideals is called the radical, where the union of two ideals is again a solvable ideal. An algebra is said to be semisimple if its radical is \{0\}. An algebra is said to be simple if it has no ideal other than L and \{0\}, and if the derived algebra (the set of the elements of L which are the result of the commutation of the two Lie elements) L not equal to \{0\}.

If the evolution operator is considered in the Wei-Norman product form as in eq. (1.3.4) the global solutions are possible in a number of cases, for example when the Lie algebra to which the Hamiltonian belongs is a solvable algebra. It has also been proved that if the Lie algebra from which the evolution operator is constructed is not a simple algebra then the equations of motion for the different sets of coefficients are decoupled.\(^{80,81}\)

Wolf and Korsch\(^{81}\) developed a theory utilizing the Levi-Malcev decomposition of finite dimensional Lie algebras and the Wei-Norman representation to the evolution operator for the application of time-dependent quantum systems. Levi-Malcev theorem states that every finite dimensional algebra L is the semidirect sum of its unique radical (i.e. the maximal solvable ideal), R and semisimple algebra S isomorphic to the factor algebra L/R. From this theorem the eq. (1.0.4) can be decomposed as

\[
id U_S /dt = H_S U_S,
\]

(1.3.5)

and

\[
id U_R /dt = (U_S^{-1} H_R U_S) U_R,
\]

(1.3.6)

where
\[ H = H_S + H_R, \quad \text{where} \quad H_S \in S \text{ and } H_R \in R. \] (1.3.7)

**U** is then written in a product form

\[ U = U_S U_R. \] (1.3.8)

From the theorem which states that every finite dimensional semisimple Lie algebra **S** can be uniquely decomposed into a direct sum of simple ideals

\[ S = S_1 \oplus \ldots \oplus S_k, \] (1.3.9)

it is found that the effort in finding **U** can be reduced by writing **U** as

\[ U_S = U_1 U_2 \ldots U_k, \] (1.3.10)

with

\[
\begin{align*}
\frac{dU_1}{dt} &= H_1 U_1, \quad \text{(1.3.11a)} \\
\frac{dU_2}{dt} &= H_2 U_2, \quad \text{(1.3.11b)} \\
&\vdots \\
\frac{dU_k}{dt} &= H_k U_k. \quad \text{(1.3.11c)}
\end{align*}
\]

In this way the problem is reduced to solving the smaller subordinate problems and **U** is factored and written in the Wei-Norman product form. The advantage in writing this form is that for solvable algebras, there exists an ordering of the basis for which the product form gives the global solution.

Alhassid and Levine\(^\text{82}\) developed a Lie-algebraic approach
to solve the dynamics in any general system. In their formalism for a specific application of linearly displaced harmonic oscillator the evolution operator is constructed as the exponential of the linear combination of the elements of six dimensional quadratic Lie algebra.

1.3.2 The time-dependent coupled cluster method: 83

The time dependent coupled cluster method is a time dependent generalization of coupled cluster theory of Coetser and Kuemmel. 83 The feature of CCM is that the evolution operator U is written as an exponential of the cluster operator S.

\[ U = \exp(S), \quad (1.3.12) \]
\[ S = S_1 + S_2 + \ldots, \quad (1.3.13) \]

and the wave function is given by

\[ \psi = \exp(S) \, |0\rangle. \quad (1.3.14) \]

The cluster operator is then expanded in terms of one, two, ... body excitation operators. The equations for S are obtained by projecting on to the Schroedinger equation. In the TDCCM the cluster operators S are chosen to be time-dependent

\[ S = \sum_{i=1}^{\alpha} S^{(i)}(t), \quad (1.3.15) \]

The TDCCM equations are obtained from projecting the wave function
on to the TDSE and left multiplying with \( \exp(-S) \)

\[
\text{i} \hbar \exp(-S) \frac{d}{dt} \exp(S) = \exp(-S) H \exp(S). \quad (1.3.16)
\]

The expression \( \exp(-S) \frac{d}{dt} \exp(S) \) is usually determined by using Hausdorff expansion,

\[
\exp(-S) \frac{d}{dt} \exp(S) = \frac{d}{dt} + S + \frac{1}{2!} [S, S] + \ldots \quad (1.3.17)
\]

This time-dependent generalization to CCM is first suggested by Hoodbhoy and Negele\(^8^4\) and by Schoenhammer and Gunnersson. Hoodbhoy and Negele employed TDCCM for determining the nuclear dynamics. Specifically truncations appropriate to strongly repulsive cores were discussed. The system they considered consists of \( n \)-particle and \( n \)-hole states. The wave function is written as

\[
|\psi> = \exp(\sum_a S_a). \quad (1.3.18)
\]

Using eq. (1.3.16) the following equations emerge

\[
<\phi| (H - i\partial/\partial t) |\psi> = 0, \quad (1.3.19a)
\]

\[
<\phi| a_p^+ a_h (H - i\partial/\partial t) |\psi> = 0, \quad (1.3.19b)
\]

\[
<\phi| a_p^+ a_p^+ a_h a_h (H - i\partial/\partial t) |\psi> = 0, \quad (1.3.19c)
\]
where \( p \) and \( h \) are occupied and unoccupied states. Writing \( S^n(t) \) in arbitrary time-dependent basis

\[
S^n(t) = \sum_{p_1, h_1} <p_1 \ldots p_n | S^n(t) | h_1 \ldots h_n> a^+_p \ldots a^+_p a^+_h \ldots a^+_h \quad (1.3.20)
\]

and

\[
d/dt \ a^+_\alpha = \sum <\beta | \dot{a} > a^+_\beta. \quad (1.3.21)
\]

The time derivative terms of eq. (1.3.19) becomes

\[
<\phi | a^+_p \ldots a^+_p a^+_h \ldots a^+_h | i\hbar/\partial \tau | \psi > = i\hbar/\partial \tau <h_1 \ldots h_n | \psi | p_1 \ldots p_n >
\]

\[
- i <p | \alpha > <\phi | a^+_p \ldots a^+_p a^+_\alpha \ldots a^+_h | \psi >.
\quad (1.3.22)
\]

Schoenhammer and Gunnerson\(^{65}\) applied TDCCM to obtain the core-level spectra of adsorbed atoms and molecules taking the coulomb repulsion in the adsorbate valence level into account. They define \( |\phi(t)> \) as

\[
|\phi(t)> = N(t) \ exp(S(t) |\phi_0>), \quad (1.3.23)
\]

where \( N(t) \) is the normalization factor. The working equations are obtained by using eq. (1.3.15), eq. (1.3.16) and eq. (1.3.17):

\[
i \dot{N}(t) = <\phi_0 | H(t) | \phi_0> N(t), \quad (1.3.24a)
\]
\[ iS^{(n)}_{\alpha_1, \ldots, \alpha_n, \mu_1, \ldots, \mu_n} = \langle \alpha_1 \ldots \alpha_n, \mu_1 \ldots \mu_n | \hat{H}(t) | \phi_0 \rangle, \]  
(1.3.24b)

where

\[ |\alpha_1 \ldots \alpha_n, \mu_1 \ldots \mu_n \rangle = a^+_{\alpha_1} \cdots a^+_{\alpha_n} a_{\mu_1} \cdots a_{\mu_n} |\phi_0 \rangle. \]  
(1.3.24c)

Eqs. (1.3.24) are \( n \) coupled nonlinear differential equations. When \( H \) contains \( m \)-body interactions, the \( n \) number of equations can be truncated after \( m \). For the system of noninteracting electrons the equation reduces to single nonlinear differential equation and it is the exact solution for the problem.

Arponen introduced a biexponential form to the evolution operator in the coupled cluster framework. Expectation values are easily obtained in this formalism. The usual \( \exp(S) \) is written as \( \exp(S)\exp(S') \), where \( S \) and \( S' \) are the excitation and deexcitation operators respectively. \( |\psi\rangle \) and \( <\psi| \) are then defined by

\[ |\psi\rangle = \exp(S) |\phi\rangle, \]  
(1.3.25a)

\[ <\psi'| = <\phi| \exp(S') \]  
(1.3.25b)

and

\[ S = \sum_{h,p} s_{ph} a^+_h a_p, \]  
(1.3.25c)

\[ S' = \sum_{h',p} s'_{ph} a^+_p a_{h'}, \]  
(1.3.25d)

where \( a^+ \) and \( a \) are the creation and annihilation operators and \( s \) and \( s' \) are the numerical amplitudes. The time dependence of the cluster operators \( S \) and \( S' \) are established by using...
time-dependent variational principle. A functional $A$ is constructed such that

$$A[\psi, \psi'] = \int dt \langle \psi'(t) | [i\hbar/\partial t - H(t)] | \psi(t) \rangle. \quad (1.3.26)$$

The TDSE equations for the bra and ket states are obtained by requiring $A$ to be stationary with respect to arbitrary variations of $\psi(t)$ and $\psi(t)$ respectively. In the $\exp(S)$ form of writing

$$A[S, S'] = \int dt \langle \phi | \exp(S'(t)) \exp(-S(t)) [i\hbar/\partial t - H(t)] | \psi(t) \rangle. \quad (1.3.27)$$

The normalization is performed by requiring $\langle \psi' | \psi \rangle = 1$. Thus

$$A = \int dt \langle \phi | \exp(S') \dot{S} | \phi \rangle - \int dt T_H(t),$$

$$= -i \int dt \langle \phi | \exp(S') S'' S | \phi \rangle - i \int dt T_H(t), \quad (1.3.28a)$$

$$T_H[S, S''] = \langle \phi | \exp(S') \exp(-S) H \exp(S) | \phi \rangle. \quad (1.3.28b)$$

The partial integration of eq. (1.3.28a) yields the equations of motion for the cluster amplitudes $S$ and $S$:

$$i \sum_j k_{ij} \dot{S}_j = \partial T_H/\partial S''_i, \quad (1.3.29a)$$

$$i \sum_j \dot{S}_j k_{ji} = -\partial T_H/\partial S_i. \quad (1.3.29b)$$

Here
This approach is restricted to systems represented by single-reference function at t=0. Extension to multi-reference systems is not trivial.

The TDCCM has been employed by Sebastian to study the ion neutralization scattering. In this system the ion is such that it has a closed shell structure with one empty orbital outside the shell, which can take up at the most two electrons from the metal surface. The $S$ operator is defined as a linear combination of all possible single particle–hole excitation operators and $S$ as a linear combination of all two particle–hole excitation operators, which transfer two electrons to the orbital of the ion from the solid. The cluster operators $S$ for $n > 2$ are neglected. For treating an ion which leaves the surface the TDCCM is a better alternative where the time-dependant Hartree Fock (TDHF) fails.

Durga Prasad has developed TDCCM theory to calculate molecular absorption spectra of systems on multi-dimensional anharmonic surfaces. The calculation involves the evolution of the doorway state $|\phi>$ under the influence of the vibrational hamiltonian of the upper surface $H$. The molecular hamiltonian is represented as

$$H(\alpha) = E_\alpha + \sum_i w_i(\alpha) a_i^+ a_i + \sum_{i} V_i(\alpha) (a_i^+ a_1) + 1/2! \sum_{i,j} V_{ij}(\alpha) (a_i^+ a_i) (a_j^+ a_j) + \ldots,$$  (1.3.30)
excitation energy. \( w \) are the frequencies and \( V \) etc. are the various anharmonicity constants. \( a \) and \( a^\dagger \) are the creation and annihilation operators of the \( I \)th mode. The doorway state is approximated by

\[ |\phi_0> = |0> \quad (1.3.31a) \]

because the anharmonicities rarely effect the vibration less state, where \( |0> \) is the vacuum state for the operator \( a \).

\[ a^\dagger_1 |0> = 0. \quad (1.3.31b) \]

The Wei - Norman product form is assumed for the evolution operator. Writing it in the normal order form and eliminating the operators which give zero acting on \( |0> \), the evolution operator is given by

\[ U(t) = \exp[ S_0 + \sum \sigma s^1_{1i} a^+_1 + \sum s^2_{1j} a^+_1 a^+_j + ...], \quad (1.3.32) \]

where

\[ S_1 = \sum \sigma s^1_{1i}, \quad (1.3.33a) \]

\[ S_2 = 1/2! \sum s^2_{1j} a^+_1 a^+_j \quad (1.3.33b) \]

and etc. The \( S \) is a complex scalar.

The time evolution of the state \( |0> \) is given by

\[ |t> = \exp(-iH_0 t)|0> = \exp(S)|0>. \quad (1.3.34) \]

The equations for the cluster amplitudes \( s_i \) etc. are obtained by

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appealing to TDSE and by projecting on to the different excited states.

\[ i\dot{S}_m = \langle m | \tilde{H}_e | 0 \rangle, \quad (1.3.35a) \]

where

\[ \tilde{H}_e = \exp(-S) H_e \exp(S). \quad (1.3.35b) \]

These are a set of coupled nonlinear differential equations to be integrated by subjecting to the initial conditions

\[ S_m(0) = 0. \quad (1.3.35c) \]

The Fourier transform of \( \exp(S_0) \) gives the molecular absorption spectra.

Very recently Sastry et al.\textsuperscript{89} developed a Lie algebraic approach for the construction of evolution operator on anharmonic potential energy surfaces without invoking any basis sets at any stage of its construction. They have constructed the evolution operator using boson ladder operators. Application to atom-diatom collisions proved the validity of the theory. Sastry et al.\textsuperscript{90} have also studied the photodissociation process using TDCCM in the boson representation formalism.

A multi-reference TDCCM has been employed by Guha and Mukherjee.\textsuperscript{91} They generalize the effective Hamiltonian theory to encompass the nonstationary situation in the TDCCM formalism. A set of nonstationary states at some initial time \( t \) are defined by

\[ \psi_k^0(t_0) = \sum_i C_{ik}(t) \phi_i, \quad (1.3.36) \]

where \( \phi \) are a set of quasi degenerate strongly interacting
functions spanning the model space. \( \psi^0 \) evolve in time according to

\[
\psi_k(t) = U(t, t_0) \psi^0_k(t_0)
\]

with \( U \) satisfying eq.(1.0.4). The evolution operator \( U \) is factorized as

\[
U_P = U_{ex} U_{n P},
\]

(1.3.38)

where \( U_n \) is the model space evolution operator and \( U \) brings the admixture of complimentary space function. \( U \) satisfies the equation

\[
\psi^0_k(t) = U_n(t, t_0) \psi^0_k(t_0)
\]

(1.3.39)

and

\[
\frac{i\partial U_n(t, t_0)}{\partial t} = H_{eff}(t) U_n(t, t_0).
\]

(1.3.40)

Here \( H \) is the model space time-dependent effective hamiltonian. Using the above relations the equation for \( U \) is written as

\[
\frac{i\partial U_{ex}}{\partial t} = H U_{ex} - U_{ex} H_{eff}
\]

(1.3.41)

with \( H \) defined by

\[
H_{eff} = [U_{ex}]^{pp \dagger} [[H_{ex}]^{pp} - i\partial U_{ex}^{pp}/\partial t].
\]

(1.3.42)

The evolution \( U_{ex}^{0P} \) is governed by

\[
\frac{i\partial U_{ex}^{0P}}{\partial t} = [H_{ex}]^{0P} - U_{ex}^{0P} H_{eff}.
\]

(1.3.43)
Here $X$ is a closed cluster operator written in the normal order and $S$ are the external operators $U$ and $U$ are taken to be normally ordered exponential ansatze (denoted by the braces in eq.(1.3.54)). The Hamiltonian of the system is considered as

$$H(t) = \sum_i h_i(t) l_i,$$

where $h_i(t)$ are time-dependent matrix elements and $l_i$ are suitable creation and annihilation operators defined in the Fock space.

The working equations are

$$i\hbar \frac{\partial S}{\partial t} = (\overline{U_{ex}H_{ex}}) - (\overline{U_{ex}H_{eff}}), \quad (1.3.46a)$$

$$i\hbar \frac{\partial X}{\partial t} = (\overline{H_{eff}U_{ex}}), \quad (1.3.46b)$$

Here the notation bar on the expression indicates that they are connected and curly bracket normal ordering of the operators. Application to 3 dimensional rotated Harmonic oscillator was presented.

1.3.3 Path integral based approaches:

In this class of methods the time evolution operator is
written as the product of several short time propagators.

\[ <i|U(nt)|j> = \sum <i|U(t)|n_1><n_1|U(t)|n_2><n_2>...<n_f|U(t)|j>. \]  

(1.3.47)

**For certain** classes of systems in which the irrelevant degrees of freedom can be treated as harmonic bath variables and for certain types interaction potentials the propagators in eq. (1.3.47) can be factorised and averaging over the bath variables can be carried out. Consequently the numerical effort does not scale exponentially with the number of degrees of freedom. On the negative side the number of paths increases exponentially with the number of intermediate states included. However, under some conditions this approach is more attractive than traditional basis set approach. Makri and co workers used it extensively to study several model problems. More recently Domcke and co workers used a similar approach to study nonadiabatic dynamics in some model systems.

1.4. SCOPE OF THE PRESENT WORK

As can be seen from the discussion above the various methods available to date, while being powerful, suffer from some lacuna or the other. The Dyson perturbation theory for example generates nonunitary approximation to the evolution operator and thus might lead to norm violation. The exponential perturbation theories such as Magnus expansion are subject to questions regarding the existence of solutions to the working equations. It
is thus desirable to develop alternative perturbation theories.

The variational methods based on linear basis set expansions are capable of providing any desired accuracy and are easy to implement. However, the expansions are slow to converge and for systems with several degrees of freedom the basis set size increases exponentially with the number of degrees of freedom in the system. In addition these approaches do not provide any intuitive picture of the physical process under study. For example it is known that the IVR is dominated by the sequence of overlapping nonlinear resonances. Energy transfer through such resonances is essentially a two body process. A straightforward linear basis set expansion does not reflect, or make use of, this information. It is thus desirable to develop approaches in which the dynamics of the system can be viewed in terms of the subsystems in a transparent manner. Development of such approaches forms the subject matter of our thesis.

The Lie-algebraic construction of the time evolution operator provides the formal framework for our discussion. We develop in Chapter II a reduction principle by which the evolution operator can be written in a non-canonical product form based on the sub-algebraic structure present in the operator space. The working equations for the coefficients of different groups of generators are decoupled in this approach even when the spectrum generating algebra is simple. This result goes beyond an earlier principle discussed by Wei and Norman and Wolf and Korsch.81 We then use this principle to develop a form of degenerate perturbation theory. The origin of norm violating intruder states is analyzed. We then present some model studies on an
harmonically driven Morse oscillator to assess the convergence properties of this perturbation theory.

We next explore the sub-algebraic structure present in the operator set present in the Fock space in Chapter III. The evolution operator constructed in the Fock space is essentially the one obtained by the TDCCM using an ordinary exponential ansatz. It turns out that different sub-algebraic sequences lead to different versions of CCM. Some of these are explicitly shown.

The CCM is a very popular approach in the electronic structure theories. It is known that the CCM provides highly accurate approximations even at a low truncations due to its exponential structure. In Chapter IV we study the dynamics of IVR in a model hydrocarbon chain to see if the similar many body structure exists that can be exploited in this class of problems. It turns out that the TDCCM with a two body cluster operator is quite accurate up to about four vibrational periods indicating the utility of TDCCM.

In the next chapter we use TDCCM to follow the dynamics of an initially prepared state in a coupled two state many mode system. The hamiltonian is taken from a linear coupling model. Unlike the IVR problem studied in Chapter IV this system is not dominated by resonances. It is known from the earlier studies that TDSCF provides a good zeroth order description for this system. We formulate TDCCM in a dynamical basis generated by TDSCF. The TDCCM at two body level improves upon the TDSCF within the time period of our study. The last chapter summarizes the conclusions of our studies.
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