SOME ASPECTS OF THE LIE-ALGEBRAIC DESCRIPTION OF ANHARMONIC DYNAMICS

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
G. MADHAVI SASTRY

SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

INDIA

MAY 1994

TO DEAR

NANNA
and My
HUSBAND

CONTENTS

CHAPTER 1:INTRODUCTION

CHAPTER 3: APPLICATIONS TO ONE-DIMENSIONAL SYSTEMS: CONVERGENCE STUDIES.

CHAPTER 4: APPLICATION TO MODEL TWO-DIMENSIONAL SYSTEMS.

CHAPTER 5: LIE-ALGEBRAIC STUDIES OF NON-ADIABATIC DYNAMICS.

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the school of chemistry, University of Hyderabad, Hyderabad, India under the supervision of Dr. M. Durga Prasad.

In keeping with the general practice of reporting scientific observations due acknowledgements have been made whenever the work described is based on the findings of other investigators.

G. Madhavi Sastry

Hyderabad
May 1994.

G. Madhavi Sastry

CERTIFICATE

Certified that the work contained in this thesis entitled: "SOME ASPECTS OF THE ALGEBRAIC DESCRIPTION OF ANHARMONIC DYNAMICS" has been carried out by Ms. G. Madhavi Sastry, under my supervision and the same has not been submitted elsewhere for a degree.

M. Durga Prasad
(Thesis Supervisor)

DEAN
School of Chemistry

ACKNOWLEDGEMENTS

With heartfelt gratitude, I wish to thank Dr. M. Durga Prasad who has introduced me to this subject and given me the opportunity to study and work in this field. His invaluable guidance and patience has helped me to understand the beauty of it. With his encouragement and counselling only I could bring out this thesis in a proper shape.

I express my sincere gratitude to Prof. E. D. Jemmis for his helpful suggestions and encouragement throughout my stay here.

I thank the Dean of the school, Prof. P. S. Zacharias and the other members of the faculty for their help. In particular, I thank Dr. A. Nangia for allowing me to use his computer.

It is a pleasure to have labmates like Ms. G. Sree Latha, Mr. G. Narahari Sastry, Mr. G. Subramanyan, Mr. G. Naga Srinivas, Mr. B. Kiran, Mr. V. Vyas and Mr. K. T. Giju with whom I had interesting discussions during my tenure. I gratefully thank all of them for their help in submitting my thesis.

With pleasure I thank all my colleagues and friends who have made my stay in this university memorable.

I thank the non-teaching staff of the School of Chemistry. I also thank the heads and staff of the computer center at the University of Hyderabad. I also thank the Organic coatings and Polymers Section of IICT for allowing me to use their computer for typing part of my thesis.

Financial assistance from the University Grants Commision (UGC) is gratefully acknowledged. Most of the calculations presented in this thesis were carried out on the Sparc station funded by DST. I thank DST for this.

I thank my parents Dr. N. Krishnamurty and Mrs. Lalitha Krishnamurty for their constant encouragement throughout my career. Their invaluable support, help and constant guidance in the most critical stages of my life has helped come this far in my career. My deepest gratitude goes to them. I also thank my younger sister Ms. N. Sharada for her great help due to which I could submit my thesis in time.

I thank my parents-in-law for their encouragement in completing my thesis. I sincerely thank my Bavagaru, Akkayyagaru, Annayyagaru, Durga, Ramana and Pavan with whom I shared some happy moments and who have helped me whenever I was in need. It is fortunate to have a brother like Sekhar who has always shown interest in my academic career over the years.

I am lucky to have a son like Kaushik whose smiling face has always put me in happy moods making me forget all my tensions. I wish I could spend more time with him.

Finally, I would like to thank my husband Mr. G. Narahari Sastry who has been very supportive and encouraging. Without whose help and invaluable guidance I could not have completed my work in time.

SYNOPSIS

In this thesis we discuss the Lie-algebraic construction of the time evolution operator [1-11] to study the dynamics on anharmonic potential energy surfaces. The essential feature of the algebraic approaches is that if the hamiltonian is an element of a Lie-algebra,

$$H = \sum_{i} h_i l_i \,, \tag{1}$$

$$[l_i \,,\; l_j] = \sum_{k} C_{ij}^{k} l_k \tag{2}$$

the time evolution operator can be parametrized as the exponential of an antihermitian element of that algebra [1,2].

$$U = \exp(X), \tag{3}$$

$$X = -X^{+} = \sum_i x_i l_i \,. \tag{4}$$

Here the coefficients C_{ij}^{k} are 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 (3) into the Schroedinger's equation for the evolution operator

$$i\, U^{-1} U = U^{-1} H U \,. \tag{5}$$

Expanding both sides of eq.(5) by the Hausdorff expansion [2] and equating the coefficients of each l_i on either side of the equation provides the required working equations. The resulting expressions are compact and provide a convenient route for generating the solution to eq.(5) either perturbatively [3] or non perturbatively [4-8].

The advantages of the algebraic method when the Lie-algebra is finite dimensional is that the number of independent variables required to define the evolution operator globally is finite, even if the underlying Hilbert space is infinite dimensional. The most general class of hamiltonians that belong to a finite dimensional Lie-algebra, other than the projection operator algebra operative in finite dimensional vector spaces, are the quadratic hamiltonians. Hence most of the studies, involving the Lie-algebraic theory have been done using the quadratic Lie-algebra [4-10]. Since most problems of practical interest require dynamics on anharmonic surfaces, the harmonic oscillator algebra cannot provide an exact solution for the evolution operator of such systems.

In this thesis we describe a way to extend the Lie-algebraic theory to describe the dynamics generated by the anharmonic hamiltonians. All anharmonic hamiltonians with fixed number of degrees of freedom are elements of a *single* infinite dimensional Lie-algebra. Thus they can all be treated on the same generic footing *irrespective* of the specific interaction potential that characterises the system. These algebras are introduced in chapter 2 along with a discussion on the difficulties encountered when a canonical representation of the evolution operator is invoked. Briefly, these consist of the following: Since the algebra is infinite dimensional, the number of independent variables required to parametrize the evolution operator is also infinity. Consequently, truncations are necessary in any practical calculation. Even then, the governing equations for the generators of the evolution operator contain infinite order polynomials of the unknown coefficients necessiating further approximations. In addition, under some exotic conditions, the existence of the solution is also questionable.

These problems can be surmounted by parametrizing the evolution operator in a non-canonical product of exponential operators. Vie and Norman [1] and Wolf and Korsche [11] have discussed a reduction principle when the algebra under consideration has an invariant sub-algebra. However the anharmonic oscillator algebra does not have any nontrivial invariant subalgebra. Consequently, the Vei-Norman and Wolf-Korsch procedure cannot be used in this case. A reduction principle to construct the time evolution operator is reviewed which we then use it to construct the tine evolution operator for a general 1-d anharmonic oscillator and later extend it to multidimensions. The evolution operator generated by the algebraic approach in the boson operator representation turns out to be the time dependent generalization (13] of the ansatz postulated by the coupled cluster Method [12] (CCM) for the anharmonic oscillators [14-17]. The concepts invoked in the CCM such as the cluster decomposition property [14 1 and the subsystem embedding condition [15] emerge naturally in the algebraic approach. It turns out that the usage of the Wie-Norman product form in which the operator sequence is chosen by areduction principle eliminates both the problems encountered in the construction of the anharnonic evolution operator by the algebraic approach.

We now briefly describe the construction of the time evolution operator for anharmonic oscillators which we discuss in chapter 2 of the thesis. For simplicity we first discuss the one dimensional systems and later extend it to the multidimensional case. The most general form of the one dimensional hamiltonian in such a case is

$$H = p^2/2m + \sum_{n=0} 1/n!\ V_n q^n \qquad (6)$$

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

$$L_0 = \{ Q_{mn} = q^m p^n \ ;\ 0 \leq m,n < \infty \} \qquad (7)$$

Equivalently, in terms of the harmonic oscillator ladder operators a and a, L_0 nay be represented as

$$L_0 = \{ A_{mn} = a^{+m} a^n \ ;\ 0 \leq m,n \leq \infty \} \qquad (8)$$

Given that H is an element of L , we can parametrize the evolution operator U in the Wei-Norman product as

$$U = \Pi \exp [S_{mn} a^{+m} a^n] \qquad (9)$$

Two ways of decomposing the infinite dimensional lie-algebra are considered from which the time evolution operators for a general anharmonic hamiltonian are constructed. To demonstrate this it is convenient to classify the operators in the infinite dimensional Lie-algebra as

a. Sets of creation operators

$$C_k = \{ a^{+(k+n)} a^k \; ; \; n \geq 1 \} \qquad 0 \leq k \leq \infty \tag{10a}$$

b. Sets of annihilation operators

$$A_k = \{ a^{+k} a^{k+n} \; ; \; n \geq 1 \} \qquad 0 \leq k \leq \infty \tag{10b}$$

c. Sets of diagonal operators

$$D_k = \{ a^{+k} a^k \} \qquad 0 \leq k \leq \infty \tag{10c}$$

Two different forms of the time evolution operator are discussed corresponding to the time dependent. generalisation of the NCCM and ECCM [12] ansatze. These are,

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

$$W_k \in C_k , \; Z_k \in D_k , \; Y_l \in A_l \tag{11a}$$

$$W_k = \Sigma S_{mk} a^{+(m+k)} a^k , \quad Y_k = \sum_m y_{mk} a^{+k} a^{(m+k)} , \quad Z_k = \sum_k S_{kk} a^{+k} a^k$$

where $m > k > 0$ and

$$U = \prod_{k=0} [\exp (W_k) \exp (Y_k) \exp (Z_k)] ;$$

$$W_k \in C_k , \; Y_k \in A_k , \; Z_k \in D_k \tag{12b}$$

The equations of motion for the different cluster amplitudes S_{m0} are obtained from eq.(5). When truncations are made in the operator set, those equations also contain finite order polynomials only. The multidimensional evolution operator is given by

$$U = U_0 \, U_1 \, U_2 \ldots \tag{13a}$$

$$U_0 = \exp \Big[\sum_{n_1 n_2 ..} S^0_{n_1 n_2 ..} \, (a_1^+)^{n_1} \, (a_2^+)^{n_2} \ldots . + S^0_{00} \Big] \tag{13b}$$

$$U_1 = \exp \Big[\sum_{\alpha} \sum_{n_1 n_2 ..} S^1_{n_1 n_2 ..;\alpha} \, (a_1^+)^{n_1} \, (a_2^+)^{n_2} \ldots a_\alpha \Big] \; \exp \Big[\sum_{\alpha\beta} S^1_{\alpha\beta} \, a^+_\alpha \, a_\beta \Big] \tag{13c}$$

The main advantage of invoking this reduction principle is that decoupled equations of notion are obtained. In the later chapters we study the convergence properties of the time dependent coupled cluster method (TDCCM). In the whole thesis we have used the names TDCCM and the algebraic method interchangeably wherever applicable.

Convergence properties of the TDCCM applied to one dimensional potential energy surfaces are studied in chapter 3. Applications to exponentially repulsive, Morse and time driven exponentially perturbed harmonic potentials [1-10] have been carried out. In all these cases, it was found that the Lie-algebraic approach converges to the numerically exact result very quickly.

In chapter 4 the time dependent coupled cluster method (TDCCM) has been applied to the photodissociation dynamics of linear triatomics using the Beswick and Jortner model [18] and the two dimensional Henon-Heils hamiltonian [19]. The autocorrelation functions and absorption spectra 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 for the photodissociation dynamics. Once again the Lie-algebraic approach showed a better convergence pattern than the linear basis set expansion approach. For the Henon-Heils system, we have studied the norm conservation for a few model systems and obtained the spectra.

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. In our applications in this chapter, we assume that only two electronic states belonging to different irreducible representations of the molecular point group and n vibrational modes, are relevant to the dynamics. The resultant hamiltonian can bo written as [20]

$$H = \sum_i |e_i\rangle \epsilon_i \langle e_i| + \omega_c a_c^+ a_c + \sum_{i \neq i} |e_i\rangle [V_c (a_c^+ + a_c)] \langle e_j|$$

$$+ \sum_t \omega_t a_t^+ a_t + \sum_{t,i} |e_i\rangle (V_t^{(i)} [a_t^+ + a_t]) \langle e_i| \qquad (14)$$

where, ω and V are the normal mode frequency and the force constants of the vibrational modes respectively. c denotes the coupling mode and t denotes the tuning mode. ϵ_i is the energy of the ith electronic state e.. a and a are the boson ladder operators operative in the vibrational subsystem. Defining the auxillary parameters,

$$V_t = 0.5 (V_t^{(1)} + V_t^{(2)}) \qquad (15a)$$

$$U_t = 0.5 (V_t^{(1)} - V_t^{(2)}) \qquad (15b)$$

the resultant hamiltonian turns out to be

$$\bar{H}_1 = \sum_{n=t,c} \omega_n a_n^+ a_n + \sum_t V_t (a_t^+ + a_t) - \epsilon \cos(\pi \sum_c a_c^+ a_c)$$

$$- \sum_t U_t (a_t^+ + a_t) \cos (\pi \sum_c a_c^+ a_c) + V_c (a_c^+ + a_c) \qquad (16)$$

We now use the coherent state operator algebra to calculate the dynamics of this system [4-11]. We parametrise the evolution operator as a product of exponentials generated by the elements of the n-dimensional harmonic oscillator algebra

$$L_n = \{ 1, a_i^+ , a_i , a_i^+ a_j^+ , a_i a_j , a_i^+ a_j \} \qquad (17)$$

Since we are particularly interested in the dynamics of the vacuum state, the evolution operator was parametrised as

$$U = \exp\left[\sum_i S_1^i a_i^+ + \sum_{i\leq j} S_2^i a_i^+ a_i^+ \right] \exp\left[- \sum_i T_1^i a_i - \sum_{i\leq j} T_2^i a_i a_i \right]$$

$$\times \exp [S_0] \qquad (18)$$

As the annihilation operators are to the extreme right the equations for the autocorrelation function simplify. The term U $\cos(\pi a_c a_c)$ U which results from the multicommutator expansion of $U^{-1} HU$ can be rearranged as $\exp(Xa_c^+)\cos(\pi a_c^+ a_c)\exp(Ya_c)$ or $\exp(Xa_c^+) \exp(Ya_c) \cos(\pi a_c^+ a_c)$ where X and Y are time dependent variables. Calculations have been performed using both the sets of equations and the results were found to be different in the two cases. We have applied the formalism to evaluate the Franck-Condon spectra of some model one dimensional systems containing only a coupling mode. As the tuning modes which modulate the electronic energy gap in the system are absent, the dependence of the coupling energy gap and the coupling constant on the spectra have been studied. We have also obtained the photoelectron spectra of a few multidimensional realistic systems.

In all our calculations we required about thirteen equations to be integrated where as the basis set expansion methods to date require an order of 20 basis [21-23] in each degree of freedom to obtain the spectra. This computational simplicity is the main attraction of the algebraic theory. The spectra obtained where in reasonably good agreement with the exact.

Calculations have also been performed using TDCCM on the mapped hamiltonian using

$$U \cdot \exp[S_m a^{+m}] \qquad (19)$$

as the time evolution operator. However the resulting equations were quite stiff and could not be integrated. As the TDCCM failed to describe the non-adiabatic dynamics of systems described by the hamiltonian eq.(14), we have applied the multireference TDCCM (MRTDCCM) to include the complete algebra of the original unmapped hamiltonian eq. (14). The advantage of MRTDCCM over single reference TDCCM is that all the electronic excitations are taken into account in MRTDCCM where as in single reference TDCCM all the electronic excitation operators involving quadratic and higher order excitations are zero for the two electronic state problem. Therefore we expect the results to be better than the single reference TDCCM. This difference between the two methods holds good for any number of electronic states in which case many of the electronic excitation operators in the exponential ansatz do not contribute in the single reference TDCCM. Two different MRTDCCM formalisms (MRTDCCM1 and MRTDCCM2) have been discussed. The Lie-algebra associated with this system is

$$L = \{ |i> <k| \prod a_{\alpha}^{+m_{\alpha}} a_{\alpha}^{n_{\alpha}} \} \vee i,k \; ; \; 0 \leq m_{\alpha}, n_{\alpha} \leq \infty \qquad (20)$$

In the case of MRTDCCM1 the operators !i> <k ! correspond to the electronic state subsystem and a. and a. correspond to the boson ladder operators of the vibrational subsystem. In MRTDCCM2 the operators !i > <k ! correspond to the combined electronic and coupling mode subsystem and the boson ladder oprators correspond to the tuning mode subsystem. A decomposition procedure is discussed similar to that discussed in chapter 2 from which the time evolution operator is constructed. We have applied the above formalism to obtain the spectra of a few realistic systems. For short time dynamics MRTDCCM performed well but the long time dynamics could not be obtained due to the stiffness of the equations.

REFERENCES

1. J. Wei and E. Norman, J. Math. Phys., 4, 575(1963)
2. **R.M.Wilcox ,J.** Math. **Phys.,8**, 962(1967).
3. **W.** Magnus, **Commun.** Pure. **Appl**. Math., 7, 649(1954).
4. (a) B. Gazdy and D.A. Micha, J. **Chem.** Phys., 82, **4926(1985);(b) E.Vilallonga** and **D.A.Micha, Int.J.Quantum Chem.** Symp,15, **653(1981);(c) J.Chem. Phys.,79**, 3794(1983).
5. J. **Kucar** and **H.D**. Meyer, J. **Chem. Phys.,90**, 5566 (1989).
6. J. Echave, F.M. Fernandez and D. A. Micha, J. Chem. Phys., 04,, 3537 (1991).
7. I. Benjamin, J. Chem. Phys., **85**, 5611(1986).
8. **H.K.** Shin, Chem. Phys. Lett., 3, 125(1969); idem, J. Chem. Phys., **81**, 1725 (1984).
9. Y. Alhassid and R. D. **Levine**, Phys. Rev. A, 18, 89 (1978); idem,J. Chem. Phys., 87, 4321 (1977).
10. Shenglu Lin, Xizhang Yi and Luzhong Cai, Chem. Phys., **160**, 163 (1992).
11. F.Wolf and **H**. J. **Korsche, Phys**. Rev. A, 37, 1934 (1988).
12. J. Arponen, Ann. Phys., **151**, 311 (1983).
13. **K**. L. Sebastian, Phys. Rev. B, 31, 6976 (1985); M. Durga **Prasad**, J. Chem. **Phys.,88**, 7005 (1988); **Proc. Ind.** Acad.Sci. (Chem. Sci.),99, 61(1987) ; Lecture notes in chemistry Vol.50 edited by D.Mukherjee p321 (Springer, Berlin, 1989) S. Guha and D. Mukherjee, Chem. Phys. Lett., 186, 84 (1991).
14. R.F. Bishop and H.G. **Kummel**, Physics Today, 40, 52(1987); F. **Coester, Nucl**. Phys. 7, 421 (1958); F.Coester and **H. Kummel**, Nucl. Phys., 17, 477(1960); J . Cizek, J. Chem. Phys., **45**, 4256(1966); J. Cizek, Adv. Chem. Phys., **14**, 35 (1969); R. J. **Bartlett**, J. Phys. **Chem.,93**, 1697 (1989).
15. D. Mukherjee, Int. J. Quant. Chem., **520**, 409 (1986).
16. R.F. Bishop and M.F. **Flynn**, Phys. Rev. A, 38, 2211 (1988).
17. U.B. **Kaulfuss** and M. **Altenbokum**, Phys. Rev. D, 33, 3658 (1986).
18. **Beswick** and Jortner, Chem. Phys., **24** ,1 (1977).
19 E. J. Heller, **Acc**. Chem. Res, 14, 386(1981).
20. H. Koppel , **W. Domcke** and L. S. **Cederbaum**, Adv. Chem. Phys., **57**, 59 (1984).

21. D. Manthe and H. Koppel, J. Chem. Phys., 93,1658 (1990);
U. Manthe and H. Koppel,Chem. Phys. Lett., 178, 36 (1991).

22. R. Schneider and W. Domcke, Chem. Phys. Lett., 1S9 61. (1989).

23. R. Schneider, V. Domcke and H. Koppel, J Chem Phys,92,1045 (1990). R. Schneider and V. Domcke, Chem. Phys. Lett., 150, 235 (1988).

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 necessiate 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.

$$\psi(t) = \sum_i C_i \phi_i \tag{1.1.1}$$

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

$$i\hbar \dot{C}_i = \sum_j H_{ij} C_j . \tag{1.1.2}$$

Several choices of basis vectors ϕ ranging from descrete 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 [2]. 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 (tine 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

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

where q_t and p. are the expectation values of position and momentum respectively, a. describes the width of the wave packet during its evolution and γ_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

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

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

$$i\hbar\, \partial\psi /\partial t = H\, \psi \qquad (1.2.3)$$

result in the following equations of motion

$$\dot{q}_t = p_t / m, \qquad (1.2.4a)$$
$$\dot{P}_t = - (\partial V/\partial q)_{q=q_t}, \qquad (1.2.4b)$$
$$\dot{\alpha}_t = -2\, \alpha_t/m -1/2\, (\partial^2 V/\partial q^2)_{q = q_t}, \qquad (1.2.4c)$$
$$\dot{\gamma}_t = i\hbar\alpha_t /m + P\, \dot{q}_t - p_t^2 /2m - V_0, \qquad (1.2.4d)$$

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 [9] 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 prevailent in the system, it cannot describe the 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 consequance 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 osccillator, Warshel and Hwang [4b] found that the GWP at thawed gaussian appoximation 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].

$$\psi = \sum_i c_i \; g_i \qquad (1.2.5)$$

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

$$\psi = P\;(q,\; q_t)g \qquad (1.2.6)$$

where P is a polynomial function of (q - q.) [7,8]. The parameters in g are obtained either variationally or non-variationally. The approach has been applied to study the photodissociation dynamics of CH_3I 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,

$$\psi(r) = \prod_i \phi_i(r_i) \exp(i\theta t), \qquad (1.3.1)$$

where ϕ (r) are the wave packets dependent on a single degree of freedom r and *6* is the overall time dependent phase factor. The general hamiltonian of a many particle system can be written as

$$H = \sum_i h_i + V \qquad (1.3.2)$$

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

$$\delta\psi \int_0^t \langle \psi \mid H - i\partial/\partial t \mid \psi \rangle \, dt' = 0 \qquad (1.3.3)$$

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

$$\delta\phi_i \int \langle \prod_i \phi_i \ (r_i) \mid \sum_i h_i + V - i\partial/\partial t \mid \prod_j \phi_j \ (r_j) \rangle \, dt' = 0$$

$$(1.3.4)$$

From the above integral the following equations emerge.

$$i\dot{\phi}_i \ (r_i) = h_i^{scf} \ \phi_i \qquad (1.3.5)$$

where,

$$h_i = \sum h_i + \int \prod_{j\neq 1} \phi_j^* \ (r_j) \ V \ \phi_j \ (r_j) \ dr_j \qquad (1.3.6)$$

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

$$\theta = \int \prod \phi_j^* (r_j)\ V\ \phi_j\ (r_j)\ dr_j . \qquad (1.3.7)$$

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 Schroodinger 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.

$$|\psi\rangle = \exp(S)\ |0\rangle \tag{1.3.8}$$

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

$$|\phi(t)\rangle = N(t)\ \exp(S(t)\ |\ \phi_0\rangle, \tag{1.3.9}$$

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

$$S\ (t) = \Sigma\ S^{(1)}_{am}\ (t)\ \psi^{+}_{a}\ \psi_{m} + \Sigma\ S^{(2)}_{abmv}\ (t)\ \psi^{+}_{a}\psi^{+}_{b}\psi_{m}\psi_{v} + \ldots\ldots$$

$$= \sum_{n=1}^{\infty} S^{(n)}\ (t), \tag{1.3.10}$$

where ψ are the annihilators of the singly occupied particle states in $|\phi_0\rangle$ and ${}_{a}\psi$ are the creation operators of the unoccupied single particle states in $|\phi_0\rangle$. S(t) satisfy the condition

$$S^{+}(t) \mid \phi_0 \rangle = 0. \qquad (1.3.11)$$

As the spectral function is determined by $\langle \phi_0 \mid \phi_t \rangle$ which can be rewritten as

$$\langle \phi_0 \mid \exp(-i\, H\, t) \mid \phi_0 \rangle = N(t), \qquad (1.3.12)$$

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

$$i\partial/\partial t\ \phi(t) = H\ \phi(t). \qquad (1.3.13)$$

Hence the following equation is obtained

$$i\ [\ \dot{N}(t) + \dot{S}(t)\ N(t)\ ]\ \exp(S(t)) \mid \phi_0 \rangle = N(t)\ H\ \exp(S(t) \mid \phi_0 \rangle \qquad (1.3.14)$$

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

$$i\ [\ \dot{N}(t) + \dot{S}(t)\ N(t)\ ] \mid \phi_0 \rangle = N(t)\ \overline{H}(t) \mid \phi_0 \rangle \qquad (1.3.15)$$

where

$$\overline{H}(t) \mid \phi_0 \rangle = \exp(-S(t))\ H\ \exp(S(t)) \qquad (1.3.16)$$

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

$$i\ \dot{N}(t) = N(t) \langle \phi_0 \mid \overline{H}(t) \mid \phi_0 \rangle \qquad (1.3.17)$$

and

$$i S_{a,m} = \langle a,m | \overline{H}(t) | \phi_0 \rangle, \quad (1.3.18)$$

where

$$|a,m\rangle = \psi^{+}_{a_1} \dots \psi^{+}_{a_n} \psi_{m_1} \dots \psi_{m_n} |\phi_0\rangle \quad (1.3.19)$$

The above formalism is applied to include only the first term in S(t) involving $\psi_a \psi_m$.

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 eqautions. The main attraction of this procedure is that the expectation value of an operator can be determined in a straight forward manner. We describe the method in the following discussion.

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

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

$$\langle v | = \langle \phi | \exp(S), \quad (1.3.20b)$$

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

$$S = \Sigma S_i c^{+}_i, \quad (1.3.21)$$

$$S' = \Sigma S'_i c_i, \quad (1.3.22)$$

where c. and c. are respectively the excitation and deexcitation operators with respect to ϕ and S and S are the numerical amplitudes. The energy eigenvalue equation is given as

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

Left multiplying by exp(-S) gives

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

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

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

$$\langle A\rangle = \langle\phi| \exp(S) A \exp(S) |\phi\rangle / \langle\phi| \exp(S)\exp(S)|\phi\rangle \qquad (1.3.25)$$

Introducing the notation

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

one obtains

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

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

$$\langle w| = \langle\phi| \exp(S) \qquad (1.3.28)$$

where

$$S = \sum S_i \, c_i \qquad (1.3.29)$$

Equations (1.3.27) and (1.3.28) imply that <A> 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).

$$T[\, S \,,0] = \langle \phi \; | 0 \exp(-S) \, H \exp (S) \, | \phi \; \rangle \qquad (1.3.30)$$

where

$$0 = \exp(S \;) \qquad (1.3.31)$$

and

$$\langle v \, | = \exp(\, S) \exp (S \,) \, | \, \phi \; \rangle \qquad (1.3.32)$$

An alternative way of writing this functional is

$$T \, [S, \, S \,] = \langle \phi \;\, | \, \exp(S \;) \exp(-S) \, H \exp(S) \, |\phi \;\, \rangle. \qquad (1.3.33)$$

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

$$\partial \, T/ \, \partial O_{.} = \langle \phi \; | c_{.} \, H \; | \phi \; \rangle = 0, \qquad (1.3.34)$$

$$\partial \, T/ \, \partial S_i = \langle \phi \;\, | O [\, H \;, \, c^{+}_{.} \,] \, | \phi \; \rangle = 0, \qquad (1.3.35)$$

from which the coefficients c. and c. 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

$$A[\psi,\psi'] = \int dt \langle \psi'(t) | [i\partial/\partial t - H(t)] | \psi(t)\rangle \qquad (1.3.36)$$

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

$$A[S, S''] = \int dt \langle \phi | e^{S''(t)} e^{-S(t)} [i\partial/\partial t - H(t)] e^{S(t)} | \phi \rangle$$

$$= \int dt \langle \phi | e^{S(t)} e^{S(t)} | \phi \rangle - \int dt\, T(t) \qquad (1.3.37)$$

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

$$i \sum_j K_{ij} \dot{S}_j = \partial T/ \partial S''_i , \qquad (1.3.38a)$$

$$i \sum_j \dot{S}''_j K_{ji} = \partial T/\partial S_i , \qquad (1.3.38b)$$

where,

$$K_{ij} [S''] = \langle \phi | c_i \exp (S'') c^+_j | \phi \rangle \qquad (1.3.38c)$$

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 fore

$$|\psi(t)\rangle = \exp\,[T_1(t) + T_2(t) + T_3(t) + \ldots]\,|\phi_0\rangle \qquad (1.3.39)$$

where ϕ_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)> in the time dependent Schroedinger equation, the equation for T (t) are obtained. The wave function is approximated as

$$\langle\, \psi(t)| = \exp\,[\; T_0(t) + T_1(t))]\;[1 + T_2(t)]\;|\phi_0\,\rangle \qquad (1.3.40)$$

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

$$H(\alpha) = E_{\alpha} + \Sigma w_{i}(\alpha)\, a_{i}^{+} a_{i} + \Sigma V_{i}(\alpha)\, (a_{i}^{+} + a_{i}) + 1/2!\, \Sigma V_{ij}\, (\alpha)\, (a_{i}^{+} + a_{i})\, (a_{j}^{+} + a_{j}) + \ldots.. \qquad (1.3.41)$$

where α represents the index of the electronic state and E_{α} is the vertical excitation energy, w. are the frequencies, V are the anharmonic coupling constants and a. and a. 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,

$$|\phi_{g}\rangle = |0\rangle. \qquad (1.3.42)$$

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

$$U\,|0\rangle = \exp\,[S]|0\rangle \qquad (1.3.43)$$

where

$$S = S_{0} + S_{1} + S_{2} + S_{3} + \ldots\ldots \qquad (1.3.44a)$$

$$S_{1} = \Sigma\, s_{i}^{1}\, a_{i}^{+} \qquad (1.3.44b)$$

$$S = 1/2!\, \Sigma\, s_{ij}^{2}\, a_{i}^{+}\, a_{j}^{+} \qquad (1.3.44c)$$

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

$$|t\rangle = \exp\,[S]\,|0\rangle. \qquad (1.3.45)$$

The equations for the cluster amplitudes S. are obtained by substituting eq. (1.3.45) in the time dependent Schroedinger equation given by

$$i\,d/dt\,|t\rangle = H_e\,|t\rangle \qquad (1.3.46)$$

Premultiplying by exp (-S) we get

$$i\,\exp(-S)\,d/dt\,\exp(S)\,|0\rangle = \exp(-S)\,H\,\exp(S)\,|0\rangle \qquad (1.3.47)$$

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

$$i\,s_m = \langle m|\,\bar{H}_e\,|0\rangle, \qquad (1.3.48)$$

where

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

which are coupled non-linear differential equations that are integrated by using the initial condition

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

The fourier transform of $\exp(S_0)$ gives the spectrum. This formalism was applied to evaluate the absorption spectra of the two dimensional Henon-Heils hamiltonian.

The time dependent coupled cluster formalism with a multireference model space was presented by Guha and Mukherjee [18]. Similar to Arponen's formalism, their work is inspired by the analysis of many body perturbation theory. The time dependent non-stationary functions $\psi_k^0(t)$ 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.

$$\psi_k^0 (t_0) = \Sigma c_{ik} \phi_i \tag{1.3.51}$$

The time evolution of ψ_k is given by

$$\psi_k (t) = U (t,t_0) \psi_k^0 (t_0), \tag{1.3.52}$$

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

$$i\partial U (t,t_0)/\partial t = H(t) U(t,t_0). \tag{1.3.53}$$

A model evolution operator U_M and a model time dependent effective hamiltonian H_{eff} are defined in the model space via

$$\psi_k^0 (t) = U_M (t,t_0) \psi_k^0 (t_0) \tag{1.3.54}$$

$$i\partial U_M(t,t_0)/\partial t = H_{eff} (t) U_M (t,t_0) \tag{1.3.55}$$

The evolution is factorised as

$$UP = U_{ex} U_M P \tag{1.3.56}$$

where P describes the projection on to model space and U_{ex} is the evolution operator defined in the complementary space. Substituting eq.(1.3.56) in eq.(1.3.53)

$$i\partial U_{ex}/\partial t = HU_{ex} - U_{ex} H_{eff} \qquad (1.3.57)$$

The PP component is given by

$$H_{eff} = [U^{PP}_{ex}]^{-1} \left([H\ U^{PP}_{ex}] - i\partial U^{PP}_{ex}/\partial t \right) \qquad (1.3.58)$$

The evolution of U^{QP}_{ex} where Q defines the projection on to virtual space is given by

$$i\partial U^{QP}_{ex} /\partial t = [\ HU_{ex}\ ]^{QP} - U^{QP}_{ex} H_{eff} \qquad (1.3.59)$$

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

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

$$U = \{\exp [S]\} \qquad (1.3.61)$$

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

$$i\partial S/\partial t\ U_{ex} = \overline{HU}_{ex} - \overline{U_{ex}\ H_{eff}} \qquad (1.3.62)$$

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

$$\{\ \overline{(U_{ex})_{cl}\ H_{eff}}\ \} = \{\ \overline{H\ U}_{ex}\ \}_{cl} \qquad (1.3.63)$$

Similarly with the external pair

$$i\partial S/\partial t = \{\overline{H\ U}_{ex}\ \}_{ex} - \{\overline{U_{ex}\ H_{eff}}\}_{ex} \qquad (1.3.64)$$

The equation for X is

$$i\partial X/\partial t = \{\ \overline{H_{eff}U_M}\ \} \qquad (1.3.65)$$

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-algbraic 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,

$$H = \sum_i h_i l_i \quad , \qquad (1.3.66)$$

$$[l_i , l_j] = \sum_k C^k_{ij} l_k \qquad (1.3.67)$$

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

$$U = \exp(X), \qquad (1.3.68)$$

$$X = -X^+ = \sum_i x_i l_i . \qquad (1.3.69)$$

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

$$i U^{-1} \dot{U} = U^{-1} H U . \qquad (1.3.70)$$

Expanding both sides of eq.(1.3.70) by the well known Hausdorff expansion [21] and equating the coefficients of each 1 on either side of the equation provides the required working equations. The resulting expressions are compact and provide a convenient route for generating the 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 dimensional. The most general class of hamiltonians that belong to a finite dimensional Lie-algebra, other than the projection operator algebra operative in finite dimensional vector spaces, are the quadratic hamiltonians. Consequently, a large body of studies have appeared in which quadratic hamiltonians which belong to the harmonic oscillator algebra have been studied by the Lie-algebraic method. We now discuss the application of the Lie-algebraic methods by various authors.

Pechukas and Light [22] discuss the Magnus [19] formula for the exponential representation of the operator solution to the Schroedinger equation for a time dependent 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

$$i\hbar \, \partial U(t,t_0)/\partial t = H(t) \, U(t,t_0), \qquad (1.3.71)$$

where $U(t,t_0)$ is the time evolution operator. If the 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

$$U(t,t_0) = \exp\{ -i \int_{t_0}^{t} dt' \, H(t')/\hbar \} \qquad (1.3.72)$$

Normally $U(t,t_0)$ is obtained by expanding it in a perturbation series obtained by iteratively integrating eq.(1.3.72)

$$U(t,t_0) = 1 - i/\hbar \int_{t_0}^{t} dt_1 \; H(t_1) \; U(t_1,t_0) \qquad (1.3.73)$$

$$= 1 - i/\hbar \int_{t_0}^{t} dt_1 \; H(t_1) + (i/\hbar)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \; H(t_1)H(t_2) + \qquad (1.3.74)$$

$U(t,t_0)$ 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 $U(t,t_0)$ is to define an operator A given by

$$\exp [\, A(t)\, J = U(t,t_0) \qquad (1.3.75)$$

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 nth 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

$$A(t) = \alpha(t)q^2 + \beta(t)p^2 + \gamma(t)\,(qp + pq) \qquad (1.3.76)$$

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 existance 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

$$U_w = \prod_k \exp\,(c_k\ l_k\ ) \qquad (1\,.3.77)$$

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]

$$U = U_S\, U_R. \qquad (1\,.3.79a)$$

and the hamiltonian is written as

$$H = H_S + H_R. \qquad (1.3.79b)$$

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

$$i\, dU_S/dt = H_S U_S, \qquad (1.3.80a)$$

$$i dU_R/dt = (U_S^{-1} H_R U_S) U_R. \qquad (1.3.80b)$$

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

$$S = S_1 \oplus \ldots\ldots\ldots\ldots \oplus S_k \qquad (1.3.81a)$$

Hence U_S is parametrised as

$$U = U_1 U_2 \ldots\ldots U_k \qquad (1.3.81b)$$

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

$$i dU_k /dt = H_k U_k, \qquad (1.3.82)$$

where $H_i \in S_i$.

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: $E = \{ X_{vm} = | v > < m | \}$
2) Set of deexcitation operators: $D = \{ Y_{mv} = |m > <v | \}$
3) Set of shift oparators: $S = \{ Z_{mn} = |m>< n |, W_{uv} = |u > <v |\}$

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

$$U = \exp(X) \exp (Y) \exp(Z+W) \qquad (1.3.78)$$

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 $\{q^2, qp + pq, p^2, q, p\}$ 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

$$H(t) = H_0 + V \qquad (1.3.83)$$

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

$$\begin{aligned} H_I(t) &= \exp[iH_0 t/\hbar]\,(\Sigma\, V(t))\, \exp[-iH_0 t/\hbar] \\ &= \Pi\, \Sigma\, f_n(t)\, x_n \qquad (1.3.84) \end{aligned}$$

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

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

which satisfies the equation

$$i\hbar\, d/dt\, U_I(t,t_0) = H_I(t)\, U_I(t,t_0) \qquad (1.3.86)$$

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

$$\alpha_1(t) = -P_1(t)/[2\zeta\, Q_1(t)]$$

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 α (t). As the equation for $\alpha_2(t)$ depends only on $\alpha_1(t)$ and the equation for $\alpha_3(t)$ depends only on $\alpha_2(t)$, these equations are analytically solvable. Therefore solving for a_1, α_2 and α_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

$$H(t) = H^{(1)}(t) + H^{(2)}(t) + V^{(12)}(t) \qquad (1.3.88)$$

where

$$H^{(i)}(t) = H_0^{(i)} + F_i(t)\, q_i + 1/2\, G_{ii}\,(t)\, q_i^2 \qquad (1.3.89a)$$

$$V^{(12)}(t) = G_{12}\,(t)\, q_1 q_2 \qquad (1.3.89b)$$

and

$$F_i(t) = (\partial V/\partial q_i)_{q_1=q_2=0} \qquad (1.3.90a)$$

$$G_{ij}(t) = (\partial^2 V/\partial q_i\, \partial q_j)_{q_1=q_2=0} \qquad (1.3.90b)$$

The time evolution operator is similarly obtained in the interaction picture from

$$U_I(t,t_0) = U_I^{(1)}(t,t_0)\, U_I^{(2)}(t,t_0)\, U_I^{(12)}(t,t_0) \qquad (1.3.91)$$

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

$$i\hbar\, \partial U_I^{(j)}/\partial t = H_I^{(j)}(t)\, U_I^{(j)}(t,t_0) \qquad (1.3.92)$$

and

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

$$= V_I^{(12)}(t)\, U_I^{(12)}(t,t_0) \qquad (1.3.93)$$

The equations of motion for the system excluding the residual coupling $V^{(12)}(t)$ are obtained as in the one-dimensional case. Because the set of operators occuring 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 sparce than the matrix obtained from expanding from the very beginning as in that case the matrix elements obatined 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,

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

$$i\hbar\ \partial U_{BL}^{(k)}/\partial t = V_c^{(k+1)}(t)\ U_{BL}^{(k)}(t,t_0) \qquad (1.3.94b)$$

$$U_{BL}^{(k)}(t_o,t_o) = 1 \qquad (1.3.94c)$$

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

$$U_L^{(k)} = \exp[\ -i\zeta_1^{(k)} q_1]\ \exp[-i\eta_1^{(k)} p_1]\ \exp[-i\zeta_2^{(k)} q_2]\ \exp[-i\eta_2^{(k)} p_2] \qquad (1.3.95)$$

where ζ and 77 are time dependent coefficients. In general after the kth transformation the evolution operator U is given by

$$U_I = U_1 U_2 U_L^{(0)} U_L^{(1)} U_L^{(2)} \ldots\ldots\ldots\ldots U_l^{(k)} U_{BL}^{(k)} \qquad (1.3.96)$$

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 collinear 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 upto 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 $(a, a^+, a^+a, a^2, a^{+2}, I)$ where a and a^+ are the harmonic oscillator ladder operators. The evolution operator in the Wei-Norman form is parametrised as

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

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

$$U = \exp[Z_1 a^+ a] \ \exp[Z_2 a^+] \ \exp[Z_3 a] \ \exp[Z_4]. \qquad (1.3.98)$$

He calls this apprach 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^2 and a^{+2} are eliminated from the hamiltonian at any given tine. The hamiltonian is separated into two parts; one involving the linear and a a terms (H.) and the other involving the quadratic terms

(H_2). The unitary operator is chosen such that

$$S = \exp [\beta (a^{+2} - a^{2})] \qquad (1.3.99)$$

and a canonical transformation of the hamiltonian is carried out.

$$S (H_1 + H_2) S^{-1} = \bar{H}_1 = A(t)a^{+}a + B(t) (a^{+} + a) + C(t). \qquad (1.3.100)$$

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 lie-algebra using a root space diagram in which the root of an operator Op is defined as

$$[n, Op] = r\ Op. \qquad (1.3.101)$$

The double photon algebra (quadratic algebra) is utilised for which they construct a matrix representation. The time evolution operator is constructed as

$$U(t) = \exp\ [ra^{+} + Ra^{+2}]\ \exp\ lv\ (n + 1/2) + 6\ I\ ]\ \exp\ [la + La\ ). \qquad (1.3.102)$$

The ground state expectation value is obtained from

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

and a squeezed state expectation value is obtained from

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

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,

$$th\ d/dt\ M\ \{\ U(t,t_0)\}\ = M\ \{\ H(t)\ \}\ M\ \{\ U\ (t,t_0)\ \} \qquad (1.3.105)$$

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 col linear 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

$$|\psi(t)\rangle = \sum c_n (t) \; U \; [l(t)] \, |\phi_n > \qquad (1.3.106)$$

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

$$U \; [l(t)] = \exp \; [\; i \; l_{.}(t) - L_{.} \;] \qquad (1.3.107)$$

where 1 (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

$$|\psi (t) > * \sum (\; c_n(t) \; U \; [l(t)] + c_n(t) \; U \; [l(t)J \; \} \; |\phi_n > \qquad (1.3.108)$$

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

$$\dot{U}\,[\,l(t)\,] = \dot{l}_i(t)\ \partial/\partial l_i\ \exp[\ i l_k(t) L_k\ ]. \qquad (1.3.109)$$

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

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

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

$$\{\ a_1^+ a_1\ , a_2^+ a_2\ , a_1^+ a_2^+\ , a_1 a_2\ , a_1^+ , a_1\ , a_2^+ , a_2\ \}$$

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 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 authors observe that the unitary transformation U acting on the elements of the algebra generates elements of the algebra again. Thus,

$$U_e^{-1} \; l_i \; U_e = \Sigma \, y_{ij} \; l_j \qquad (1.3.111)$$

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

$$U_e^{-1} \; H \; (l_i) \; U_e = H \; (U_e^{-1} \; l_i \; U_e). \qquad (1.3.112)$$

Instead of the coefficients x. in the exponential ansatz, the mixing coefficients y. . are now to be determined so as to optimize the convergence in 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

$$H_{eff} = \Sigma \, h_i \; x_i , \qquad (1.3.113)$$

where x belongs to the lie-algebra L to which the hamiltonian belongs. The matrix elements of H are given by

$$(H_I)_{jk} = \langle \chi_j \mid H - H_{eff} \mid \chi_k \rangle , \qquad (1.3.114)$$

where χ_i are given by

$$x_j'(t) = \sum_{k=1}^{n} G_{jk}(t)\, x_k, \tag{1.3.115}$$

where x. also belong to L and G are the functions of tine satisfying linear equations of motion. Another matrix F_{ik} is defined as

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

Hence the matrix 6 satisfies

$$i\hbar\, \partial G/ \partial t = F\, G, \tag{1.3.117}$$

χ_k are related to the time dependent coefficients by

$$\phi(t) = \sum c_k(t)\, \chi_k \tag{1.3.118}$$

where ϕ (t) is related to the state of the system v(t) by

$$\psi(t) = U_{eff}(t, t_0)\, \phi(t). \tag{1.3. 119}$$

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

$$i\hbar\, dC/dt = H_I\, C. \tag{1.3.120}$$

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

Lin et al [33] have applied the six-dimensional quadratic Lie-algebra to study the scattering of ^4He and ^3He particles from the (001) face of LiF crystal. They use the time evolution operator of the form

$$U_{\alpha\beta}(t) = \exp\,[T_{\alpha\beta}(t)] \qquad (1.3.121)$$

where

$$T_{\alpha\beta}(t) = -i/\hbar\,[\,U^{(1)}_{\alpha\beta} I + U^{(2)}_{\alpha\beta} a^{+} + U^{(2)*}_{\alpha\beta} a + U^{(3)}_{\alpha\beta} a^{+} a + U^{(4)}_{\alpha\beta} a^{+2} + U^{(4)*}_{\alpha\beta} a^{2}\,]. \qquad (1.3.122)$$

Similar to the other applications of the Lie-algebaric 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 ψ (x,t) as

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

$$= \prod_{k=1}^{m} \exp\,[i\alpha_k(t) A_k]\,\phi_n(x) \qquad (1.3.123)$$

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

$$\Psi(x,t) = \sum_n a_n(t)\,\psi_n(x,t)$$

$$= U(t) \sum_n a_n(t)\, \phi_n(x)$$

$$= U(t)\, f(x,t). \qquad (1.3.124)$$

The effective hamiltonian is defined as

$$H_{eff} = \bar{H} + \sum_{k=1}^{m} \dot{\alpha}_k \bar{A}_a , \qquad (1.3.125)$$

where

$$\bar{A}_k = [\prod_{l=1}^{k-1} \exp\,(i\alpha_l\, A_l)\,]^{+}\; A\; [\prod_{l=1}^{k-1} \exp\,(i\alpha_l\, A_l)\,] \qquad (1.3.126)$$

and

$$\bar{H} = U^{+}\, H\, U. \qquad (1.3.127)$$

The coefficients a satisfy the equations of motion

$$i\, \dot{a}_n = \sum_l \langle^{-} \phi_n \mid H_{eff} \mid \phi_l \rangle\, a_l . \qquad (1.3.128)$$

α (t) are determined so that the convergence of Ψ (x,t) is optimal from the variational principle stating

$$\sum_n (n + 1/2)^j \mid a_n \mid = \langle f \mid H_0^j \mid f \rangle = \min \qquad (1.3.129)$$

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

$$\langle \psi \mid U\, H_0\, U^{-1} \mid \psi \rangle = \langle f \mid H_0 \mid f \rangle = G\,(\alpha\; , \psi). \qquad (1.3.130)$$

According to the variational principle

$$\partial G / \partial \alpha_k = 0 \qquad (1.3.131)$$

from which they determine a . In their calculations, they use the harmonic oscillator eigenfunctions for ϕ_n and A_κ. 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

$$XP = 1/2 (xp + px) \qquad (1.3.132)$$

and

$$H_0 = 1/2 (P^2 + Q^2). \qquad (1.3.133)$$

The time evolution operator is chosen as

$$U (t) = \exp (-ix_t p) \exp (ip_t x) \exp (ib_t x^2) \exp (ia_t XP) \exp (i\gamma_t H_0) \\ X \exp (i\delta_t), \qquad (1.3.134)$$

hence the time dependent basis become

$$\psi_n (x,t) = \exp [a_t/2 + ib_t(x-x_t)^2 + ip_t(x-x_t) + i(n + 1/2)\gamma_t + i\delta_t] \\ X \phi_n [\exp(at) (x-x_t)] \qquad (1.3.135)$$

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

$$< A > = \mathrm{Tr}\ (p\ A), \qquad (1.3.136)$$

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

$$S(p) = -\mathrm{Tr}\ (p \ln p). \qquad (1.3.137)$$

The state of maximal entropy corresponds to

$$\rho = \exp\ [\ -\sum_{r=0} \lambda_r\ A_r\ ] \qquad (1.3.138)$$

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

Tr (p) = 1 (normalisation condition)

and

$$< A > = \mathrm{Tr} (\rho A_r) \; ; \; r = 1,n. \tag{1.3.139}$$

Substituting the normalisation condition in the equation for *p*

$$\exp (\lambda_0) = \mathrm{Tr} [\exp (-\sum_{r=1} \lambda_r A_r)] \tag{1.3.!40}$$

only when the sum in the above equation converges does the normalised density operator of maximal entropy exists. The S *lp]* at the maximum is

$$S \; [\rho] = \lambda_0 + \sum_{r=1} \lambda_r < A_r > . \tag{1.3.141}$$

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

$$- \ln \rho \, (t) = \sum_{r=0} \lambda_r \, (t) \, A_r \, . \tag{1.3.142}$$

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

$$\rho(t) = U \, (t,t_0) \, \rho \, (t_0) \, U^+ \, (t,t_0). \tag{1.3.143}$$

The equations of motion are

$$i \hbar \, \partial U(t,t_o)/\partial t = H \, U(t,t_0) \qquad (1.3.144a)$$

$$i\hbar \, \partial \rho(t)/\partial t = [H, \rho(t)]. \qquad (1.3.144b)$$

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

$$i\hbar \, \partial \ln \rho(t)/\partial t = [H, \ln \rho(t)]. \qquad (1.3.145)$$

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

$$I = -\ln (\rho) \qquad (1.3.146)$$

where,

$$I = \sum_r \lambda_r A_r \qquad (1.3.147)$$

where A are the Lie-elements and λ are constants. The equations of motion are obtained from

$$i \dot{I} = [H, S]. \qquad (1.3.148)$$

Substituting the equation for I in the above equation results in

$$i \sum \dot{\lambda}_r A_r = \sum_r [H , A_r \lambda_r]$$

$$= \sum \lambda_r [H , A_r]. \qquad (1.3.149)$$

Let

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

Hence,

$$i \sum_r \lambda_r A_r = \sum_{r,s} A_s G_{sr} \lambda_r = \sum_r A_r G_{rs} \lambda_s \qquad (1.3.150a)$$

$$i \dot{\lambda}_r = \sum_s G_{rs} \lambda_s . \qquad (1.3.150b)$$

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 anharmopic 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 sytem and later extend it to the multidimensional case. The most general form of the one dimensional hamiltonian in such a case is

$$H = p^2/2m + \sum_{n=0} 1/n! \, V_n q^n . \qquad (1.4.1a)$$

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

$$L_0 = \{ Q_{mn} = q^m p^n \ ; \ 0 \le m,n \le \infty \} \qquad (1 .4.2a)$$

Transforming to the harmonic oscillator ladder operator representation, we have

$$H = \sum_{m,n} h_{mn} \, a^{+m} \, a^n \qquad (1.4.1b)$$

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

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

$$a = [\ (m\omega)\, q - i\ (1/m\omega)\, p\ ]/ \sqrt{2}\, \hbar$$

where ω is an arbitrary parameter . In this representation L is given by

$$L_0 = \{A_{mn} = a^{+m}\, a^{n}\ ;\ 0 \le m,n \le \infty\} \qquad (1.4.2b)$$

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

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

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

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 ≥ 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 seperate 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 Henon-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

1. E. Schroedinger, Ana. Physik., 79, 361 (1926).
2. R. Kosloff, J. Phys. Chem., 92, 2087(1988); R. E. Wyatt, Adv. Chem. Phys., 73, 231 (1989).
3. a)E. J. Heller, J. Chem. Phys., 65, 1544 (1975);b) E. J. Heller, Acc. Chem. Res, **14,** 386(1981).
4. a)D.J. Huber and E.J. Heller, J. Chem. Phys., 87, 5302(1987).b) A. Warshel and J. K. Hwang, J. Chem. Phys., 82, 1756 (1985).
5. E. J. Heller, J. Chem. Phys., 94, 2723(1991).
6. D.J. Huber, S. Ling, D.G. Imre and E.J. Heller, J. Chem. Phys., OO, 7317(1989).
7. S. Y. Lee and E. J. Heller, J. Chem. Phys.,76, 3035 (1982).
8. R. D. Coalson and M. Karplus, Chem. Phys. Lett.,90, 301 (1982).
9. a) R. D. Coalson and M. Karplus, J. Chem. Phys., 93, 3919 (1990); b) F. Arickx, J. Broeckhove, W. Coeme and P. Van Leuven, Int. J. Quantum Chem. S 20, 471 (1986).
10. J. A. Beswick and J. Jortner, Chem. Phys., 24 ,1 **(1977).**
11. a) R. B. Gerber and M. A. Ratner, J. Phys. Chem., 90, 20 (1986);b) A. D. Hammerich, R. Kosloff and M. A. Ratner, Chem. Phys. Lett., **171,** 97 '(1990);c) M. Messina and R. D. Coalson, J. Chem. Phys., 85, 4015 (1989); d) U. Manthe, H. D. Meyer and L. S. Cederbaum, J. Chem. Phys., 97, 3199 (1992); e) M Durga Prasad, Chem. Phys. Lett., 194, 27 (1992).
12. a)A. D. Mclachlan, Mol. Phys., 8, 39 (1964); b) K. Goeke and P. G. Reinhardt eds., Lecture notes in Physics, Vol. **171,** Time dependent Hartree Fock and beyond (Springer Berlin, 1982).

13. K. Schonhammer and O. Gunnarson, Phys. Rev. B, 18, 6606 (1978).

14. P. Hoodbhoy and J. W. Negele, Phys. Rev. C, 19, 1971 (1979).

15. J. Arponen, Ann. Phys., 151, 311 (1983).

16. K. L. Sebastian, Phys. Rev. B, 31, 6976 (1985).

17. M. Durga Prasad, J. Chem. Phys.,88, 7005 (1988); Proc. Ind. Acad.Sci. (Chem. Sci.),99, 61(1987) ; Lecture notes in chemistry Vol.50 edited by D.Mukherjee p321 (Springer, Berlin, 1989)

18. S. Guha and D. Mukherjee, Chem. Phys. Lett., 186, 84 (1991).

19. W. Magnus, Commun. Pure. Appl. Math., 7, 649(1954).

20. a)J. Wei and E. Norman, J. Math. Phys., 4, 575(1963);b) F. Wolf and H. J. Korsche, Phys. Rev. A, 37, 1934 (1988).

21. R.M.Wilcox, J. Math. Phys.,8, 962(1967).

22. P.Pechukas and J.C.Light,J. Chem. Phys.,44, 3897(1966).

23. G.Sree latha and M.Durga Prasad, Theor. Chim. Acta, 86, 511 (1993).

24. (a) B. Gazdy and D.A. Micha, J. Chem. Phys., 82, 4926(1985);(b) E.Vilallonga and D.A.Micha, Int.J.Quantum Chem. Symp,15, 653(1981);(c) idem, J.Chem. Phys.,79, 3794(1983)

25. D.Secrest and B.R. Johnson, J.Chem. Phys., 4,5, 4556(1966).

26. D.A. Micha Int. J. Quantum Chem.,23, 551(1983)

27. J.A. Recamier, D.A. Micha and B. Gazdy, Chem. Phys. Lett., 110, 383 (1985); idem, J. Chem. Phys., 8S, 5093 (1986).

28. H.K. Shin, Chem. Phys. Lett., 3, 125(1969); ibid, J. Chem. Phys., 81, 1725 (1984).

29. I. Benjamin, J. Chem. Phys., 85, 5611(1986).

30. J.Yuan and R. Gilmore, J. Chem. Phys., 86, 130(1987).

31. S. Shi and H.A. Rabitz, J. Chem. Phys.,88, 7508 (1988).

32. J. Echave, F.M. Fernandez and D. A. Micha, J. Chem. Phys., 94, 3537 (1991).

33. Shenglu Lin, Xizhang Yi and Luzhong Cai, Chem. Phys., 160, 163 (1992).

34. J. Kucar and H.D. Meyer, J. Chem. Phys.,90, 5566 (1989).

35. Y. Alhassid and R. D. Levine, Phys. Rev. A, 18, 89 (1978); idem, J. Chem. Phys., 87, 4321 (1977).

CHAPTER 2

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

2.1 INTRODUCTION

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

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

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

$$H = \Sigma h_i l_i \,, \tag{2.1.1a}$$

$$[l_i , l_j] = \Sigma_k C^k_{ij} l_k , \tag{2.1.1b}$$

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

$$U = \exp(X), \tag{2.1.2a}$$

$$X = -X^{+} = \underset{i}{Z}\; x \quad \mathrm{l} \quad . \tag{2.1.2b}$$

Here the coefficients C are called the structure constants of the algebra.

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

$$i\; U^{1}\; U = U^{1}\; H\; U \; . \tag{2.1.3}$$

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

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

$$\psi = U_e\,\phi. \tag{2.1.4a}$$

The model wave function then satisfies the equation

$$i\phi = (U_e^{-1} H U_e - iU_e^{-1} U_e)\,\phi. \tag{2.1.4b}$$

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

$$U_e = \exp\left[\,\sum x_i l_i\,\right] \;;\quad l_i \in L_H = \{q,p,q^2,p^2,qp+pq,1\} \tag{2.1.5}$$

Here q and p are the coordinate and momentum operators. Given that 1 belong to an algebra, it is possible to define an intermediate reference hamiltonian H by

$$i\,\dot{U}_e = H_e\,U_e, \tag{2.1.6}$$

where H_e is also an element of L_H. Consequently, eq(2.1.4b) can be rewritten as

$$i\phi = U_e^{-1} (H - H_e) U_e \phi. \qquad (2.1.7)$$

The model wave function ϕ is now expanded in terms of the basis vectors χ of the **Hilbert** space,

$$\phi = \sum_n C_n \chi_n . \qquad (2.1.8)$$

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

$$U_e^{-1} l_i U_e = \sum y_{ij} l_j . \qquad (2.1.9)$$

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

$$U^{-1} H(l) U = H(U^{-1} l_i U_e). \qquad (2.1.10)$$

Instead of the coefficients x. in the exponential ansatz, the mixing coefficients y. . are now to be determined so as to optimize the convergence in eq(2.1.10).

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

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

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

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

Sec. 2.2c. Finally, in the last section, we conclude with a general discussion of the method.

2.2. METHODOLOGY

2.2a. The Algebra of the Anharmonic Oscillators.

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

$$H = p^2/2m + \sum_{n=0} 1/n! \; V_n q^n . \qquad (2.2.1a)$$

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

$$L_0 = \{ Q_{mn} = q^m p^n \; ; \; 0 \leq m,n \leq \infty \} \qquad (2.2.2a)$$

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

$$[q^3, p^2] = 6 \hbar^2 q + 6 i \hbar q^2 p . \qquad (2.2.3a)$$

The commutator of the second term in this operator with q^3 once again gives

$$[q^2p,q^3] = -3i\hbar q^4 \,, \tag{2.2.3b}$$

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

$$[q^2p,p^2] = 2\hbar^2 p + 4i\hbar q p^2 \tag{2.2.3c}$$

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

$$H = \sum_{m,n} h_{mn}\, a^{+m}\, a^{n} \,. \tag{2.2.1b}$$

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

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

$$a = [\ (m\omega)\, q - i\ (1/m\omega)\, p\ ]/ \sqrt{2}\ \hbar$$

where to is an arbitrary parameter. In this representation L_0 is given by

$$L_0 = \{A_{mn} = a^{+m}\, a^n \;;\; 0 \le m,n \le \infty\}, \qquad (2.2.2b)$$

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

$$U = \exp[S], \qquad (2.2.4a)$$

$$S = \sum_{m,n=0}^{\infty} S_{mn}\, a^{+m}\, a^n \;;\quad S_{mn} = -\, S^*_{nm}. \qquad (2.2.4b)$$

This representation runs into two difficulties. To begin with, even when the summation for S operator in eq.(2.2.4) is restricted to some finite values of m and n (m,n $\gtrsim$ 2), the Hausdorff expansion gives a non-terminating series. To see this consider a truncation of S with only two terms in it, S_{30} a and S_{03} a and one term in H containing only a. Then,

$$U^{-1}\, H\, U \sim \exp[-\, S_{30}\, a^{+3} + S_{03}\, a^3]\; a\; \exp[S_{30}\, a^{+3} - S_{03}\, a^3]$$

$$= a + 3S_{30}\, a^{+2} + 3S_{30}\, S_{03}(6a + 6a^{+}aa)/2! +$$

$$18S_{30}\, S_{03}\, (3S_{30}\, a^{+2} + 6S_{30}\, a^{+3}a + 3S_{03}\, a^4 + 6a^{+2})/3! + \ldots \qquad (2.2.5)$$

Note that at each alternate order a^2 term is once again generated. Thus, even when the operator set in eq.(2.2.4b) is restriced to a few terms, the coefficients of all operators in U HU would contain infinite order polynomials in S_{mn}. Since little is known about the magnitudes of S *appriori*, it becomes difficult to evaluate them numerically without invoking some further approximations. The second problem with the representation (2.2.4) is that under some conditions the governing equations are not well defined. This can be seen by considering

$$U^{-1}\, d/dt\; U \sim \exp\left[-S_{30}a^{+3} + S_{03}a^{3} \right] d/dt\, \exp\left[S_{30}a^{+3} - S_{03}a^{3} \right]$$

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

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

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

$$+ (a^{+}a^{4} + a^{3})S_{03} + S_{30}a^{+3} + S_{03}a^{3} \} \right] + \ldots\ldots\ldots$$

$$= d/dt + 54/3!\,(\dot{S}_{30} + 2\dot{S}_{30}S_{03}S_{30} + 2\dot{S}_{03}S_{30}^{2} + \ldots)\, a^{+3} + . \tag{2.2.6}$$

As can be seen, the coefficient of the a^{+3} operator is $\overset{*}{S}_{30}$ multiplied by a polynomial function of S_{30} and S_{03}. If this function were to become zero at some point of the evolution, then S_{30} would not be defined.

Both these problems arise because the ansatz (2.2.4) treats stepup and stepdown operators on equal footing. As a consequence, the multi commutator expansion becomes a non-terminating series. If these two sets of operators are disentangled and written as seperate exponentials these difficulties would not appear. This provides the motivation for invoking a Wei-Norman product form for the evolution operator. In Sec. 2.2b we discuss a reduction principle by which such a disentanglement of operators can be achieved in a systematic fashion by exploiting the sub-algebra structure of L_0 and in Sec.2.2c we will use it to construct the evolution operator for the 1-d anharmonic oscillators. Extensions to multidimensional AHOs will be presented in Sec.2.2d.

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

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

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

$$C_0 = \{ l_i^0 \} = L_0 - L_1 . \subset L_0 . \tag{2.2.7a}$$

If U is parametrized as

$$U = U_0 \, U_R , \tag{2.2.7b}$$

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

$$X_0 = \sum_i x_i^0 l_i^0 \quad ; \quad l_i^0 \in C_0, \qquad (2.2.7(1)$$

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

$$i\dot{U}_R = H_R \ U_R, \qquad (2.2.8a)$$

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

Note that by eq. (2.2.8), U_R is generated by the effective **hamiltonian** H_R. Thus an exponential representation of U is generated by the operator basis of the algebra to which H_R belongs. In general, H_R belongs to L_0, since by Hausdorff expansion eq. (2.2.8b) gives

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

where h_i functions are transformed hamiltonian matrix elements. These and f are functions of the structure constants of the algebra. However it is possible to restrict H_R to L_0 by requiring that all the coefficients of the l_i^1 operators in H_R vanish. With this it would now be possible to parametrize U_R strictly in terms of the operators of L_0 alone. Since C_0 does not contain any of the operators belonging to L, this leads to a product form of U in which the governing equations for the coefficients of the operators in C_0 are decoupled from the coefficients of the operators in L_1. Since the number of x variables is equal to the number of operators l in C_0 by definition (eq.(2.2.7d), these equations can always be satisfied. Formally this can be written as,

$$(U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0) l_i^0 = 0 \qquad (2.2.8d)$$

which becomes the working equation for U_0. With eq. (2.2.8d) satisfied and consequently H_R restricted to L_1, U_R can now be parametrized as

$$U_R = \exp (X_1) \qquad (2.2.8e)$$

$$X_1 = \sum_i x_i^1 l_i^1 ; \qquad l_i^1 \in L_1 . \qquad (2.2.8f)$$

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

$$U = \prod_k U_k , \qquad (2.2.9a)$$

$$U_k = \exp (X_k) \qquad (2.2.9b)$$

$$X_k = \sum_k x_i^k l_i^k \; ; \; l_i^k \in C_k = L_k - L_{k+1} . \qquad (2.2.9c)$$

The decoupled equations of motion for the coefficients of the generators are given by

$$(U_k^{-1} \bar{H}_k U_k - i U_k^{-1} \dot{U}_k)_{l_i^k} = 0, \qquad (2.2.10a)$$

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

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

$$H = \omega a^+a + f(a^+ + a) + g(a^+a^+ + aa). \qquad (2.2.11)$$

This hamiltonian is an element of the harmonic oscillator algebra $L_n = \{ a, a \ , a \ a, a \ a \ , aa, 1 \}$. This algebra has several sequences of sub-algebras. We discuss one of them here.

$$L_H \supseteq L_1 \supseteq \ldots\ldots. \qquad (2.2.12a)$$

with

$$L_1 = \{ a^+a, \ aa, a \ , 1 \}. \qquad (2.2.12b)$$

It can readily be verified that L. is closed under commutation. The difference of L_0 and L. is given by

$$C_0 = L_H - L_1 = \{ a^+, \ a^+a^+ \}. \qquad (2.2.12c)$$

Thus in the first step we write U as the product of two exponential operators U_0 and U_R where U_0 is generated by the operators in C_0 alone and U_R is generated by the operators in L alone.

$$U = U_0 \, U_R \tag{2.2.13a}$$

$$U_0 = \exp(S) \tag{2.2.13b}$$

$$S = S_{10} \, a^+ + S_{20} \, a^+ a^+ . \tag{2.2.13c}$$

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

$$i \, \dot{U}_R = H_R \, U_R \tag{2.2.14a}$$

where,

$$H_R = U_0^{-1} \, H \, U_0 - i U_0^{-1} \, \dot{U}_0 . \tag{2.2.14b}$$

Evaluating these terms we find

$$
\begin{aligned}
U_0^{-1} \, H U_0 &= \exp(-S) \, H \exp(S) \\
&= H + [H,S] + [[H,S], S]/2! + \ldots \\
&= \omega a^+ a + f(a^+ + a) + g(a^+ a^+ + aa) + \omega S_{10} a^+ + 2\omega S_{20} a^+ a^+ \\
&\quad + f S_{10} + 2f S_{20} \, a^+ + 2g S_{10} \, a + 4g S_{20} a^+ a + 2g S_{20} + \\
&\quad + (2g S_{10}^2 + 4g S_{20} S_{10} \, a^+ + 8g S_{10} \, S_{20}^2 \, a^+ a^+) /2!
\end{aligned}
\tag{2.2.15a}
$$

and

$$iU_0^{-1}\,\dot{U}_0 \;=\; i\dot{S}_{10}\,a^+ + i\dot{S}_{20}\,a^+a^+. \tag{2.2.15b}$$

To achieve the decoupling of the equations of motion of U_0 and U_R we need to set the coefficients of the operators belonging to C in H_R as zero (Cf. eq.(2.2.8)). This is achieved by setting

$$i\dot{S}_{10} = f + \omega\,S_{10} + 2fS_{20} + 4gS_{20}\,S_{10} \tag{2.2.15c}$$

$$i\dot{S}_{20} = g + 2\omega\,S_{20} + 4gS_{20}^2. \tag{2.2.15d}$$

With these equations satisfied, H_R takes the form

$$H_R = (\,\omega + 4gS_{20}\,)\,a^+a + (f + 2gS_{10}\,)a + g\,aa$$

$$+ (fS_{10} + 2gS_{20} + gS_{10}^2\,). \tag{2.2.15e}$$

Note that this operator contains the operators belonging to L = {a a,a,aa,1} only. To continue further we note that L = {a a,a,aa} is a sub-algebra of L_1. The difference of L_1 and L_2 is the identity operator. Thus, the time dependent C-function in H_R can be factorized in U_R to give

$$U_R = U_c\,U_1, \tag{2.2.16a}$$

$$U_c = \exp\,(S_{00}\,), \tag{2.2.16b}$$

$$i\dot{S}_{00} = fS_{10} + 2gS_{20} + gS_{10}^2. \tag{2.2.16c}$$

Further, $L_3 = \{ a, aa \}$ is a sub-algebra of L_2. Thus U_1 can be parametrized as

$$U_1 = U_D\, U_x \tag{2.2.17a}$$

$$U_D = \exp(\, S_{11}\, a^+ a\,) \tag{2.2.17b}$$

$$U_x = \exp(\, S_{01}\, a + S_{02}\, aa\,). \tag{2.2.17c}$$

The governing equations for these are obtained similarly and give

$$i\dot{S}_{11} = \omega + 4g\, S_{20} \tag{2.2.18a}$$

$$i\dot{S}_{01} = f + 2g\, S_{10} \tag{2.2.18b}$$

$$i\dot{S}_{02} = g\,. \tag{2.2.18c}$$

The full evolution operator is thus given by

$$U = \exp(\, S_{10}\, a^+ + S_{20}\, a^+ a^+\,)\, \exp(S_{00})\, \exp(S_{11} a^+ a)$$

$$\exp(S_{01} a + S_{02} aa). \tag{2.2.19}$$

Note that the equations of motion for S and S_{20} are decoupled from the rest of the coefficient set. Similarly while S_{00} depends parametrically on S_{10} and S_{20}, it is decoupled from S_{11}, S_{01} and S as was desired. Note that the operator sequence in eq.(2.2.19) is different from that used by earlier authors [2-8]. For example, Benjamin [5] uses the operator ordering

$$U = \exp(Z_1 a^+ a)\ \exp(Z_2\ a^+ a^+)\ \exp(Z_3 a^+)\ \exp(Z_4 a)\ \exp(Z_5\ aa)\ \exp(Z_6).$$

As a consequence, his equations of motion for the coefficients of a and a a depend explicityly on the coefficient of a a. This is in contrast to our approach where the equation for the coefficients of a a and a are decoupled from the coefficient of a a.

2.2c. Evolution operator for one dimensional AHO.

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

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

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

a. Sets of creation operators

$$C_k = \{\ a^{+(k+n)}\ \ a^{k}\ \ ;\ \ n \geq 1\ \}\quad 0 \leq k \leq \infty. \tag{2.2.21a}$$

b. Sets of annihilation operators

$$A_k = \{ a^{+k} a^{k+n} \; ; \; n \geq 1 \} \qquad 0 \leq k \leq \infty . \qquad \textbf{(2.2.21b)}$$

c. Sets of diagonal operators

$$D_k = \{ a^{+k} \; a^k \} \qquad 0 \leq k \leq \infty . \qquad \textbf{(2.2.21c)}$$

Consider now the set of operators $L = L_0 - C_0$. Other than the identity operator in D , all other operators in this set contain *at least* one annihilation operator. **Consequently**, their **commutators** also contain at least one annihilation operator. To see this we evaluate the commutator of two typical elements of L_1.

$$[a^{+m} a^n \, , \, a^{+p} a^q \,] = a^{+m} [a^n \; a^{+p}]a^q + a^{+p}[\, a^{+m} \, a^q \,]a^n \qquad (2.2.22a)$$

$$= \sum_{r=0}^{Min(n,p)} a^{+(m+p-r)} \, a^{(n+q-r)} \, {}^{n}C_r \, {}^{p}C_r \; - \sum_{r=0}^{Min(m,q)} a^{+(m+p-r)} \, a^{(n+q-r)} \, {}^{m}C_r \, {}^{q}C_r . \qquad \textbf{(2.2.22b)}$$

Since n and q are at least 1, and r is at most either q or n, the terms with non-zero coefficients contain at least one a on the right. Thus L. is closed under commutation and hence is a Lie-algebra. **Consequently**, the time evolution operator can be factorized as

$$U = U_0 \; U_R, \qquad (2.2.23a)$$

where U_0 and U_R are exponential operators generated by the operators in C and L **respectively**.

$$U_0 = \exp \left[\sum_m S_{m0} \; a^{+m} \right] \qquad (2.2.23b)$$

$$U_R = \exp \left[\sum_m r_m \; X_m \right] ; \qquad X_m \in L_1 . \qquad [2.2.23c)$$

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

$$U_R = U_{D0} \; U_R^{'} \qquad (2.2.23d)$$

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

$$U_{D0} = \exp (S_{00}) \qquad (2.2.23e)$$

$$U_R^{'} = \exp \left[\sum_m r_m^{'} \; X_m^{'} \right] \quad ; \; X_m^{'} \in L_1^{'} . \qquad (2.2.23f)$$

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

$$U = U_0 \; U_{D0} \; U_R^{'} \qquad (2.2.23g)$$

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

The last set in this sequence of sub algebras is

$$L_\infty = \bigcup_{k=1} A_k . \tag{2.2.24a}$$

This can be further decomposed as follows

$$L_1^{''} = L_\infty - A_0 \tag{2.2.24b}$$

$$L_{k+1}^{''} = L_k^{''} - A_k . \tag{2.2.24c}$$

Thus the evolution operator after complete **factorization** reads as

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

$$W_k \in C_k ,\; Z_k \in D_k ,\; Y_l \in A_l \tag{2.2.25a}$$

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

where $m > k \geq 0$.

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

Returning to the equation of motion for U_0

$$(U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0)_{1}{}^{0}_{i} = 0 \qquad (2.2.26a)$$

we find

$$i U_0^{-1} \dot{U}_0 = i \exp [\sum_m - S_{m0} a^{+m}] d/dt \exp [\sum_m S_{m0} a^{+m}]$$

$$= i\, d/dt + i \sum \dot{S}_{m0} a^{+m} , \qquad (2.2.26b)$$

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

$$U_0^{-1} H U_0 = H + \sum S_{m0} [H, a^{+m}] + 1/2! \sum S_{m0} S_{n0} [[H, a^{+m}], a^{+n}]$$

$$+ \ldots\ldots\ldots \qquad (2.2.26c)$$

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

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

$$U|0\rangle = \exp\,[\sum_m S_{m0}\, a^{+m} + S_{00}\,]\ |0\rangle, \tag{2.2.27a}$$

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

$$U|1\rangle = \exp\,[\sum_{m=1} S_{m0}\, a^{+m} + S_{00}\,]\ \exp[\sum_{m=2} S_{m1}\, a^{+m}\, a\,]\ \exp[S_{11} a^{+} a]\ |1\rangle. \tag{2.2.27b}$$

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

A second sequence of sub algebras to L_0 which yield the evolution operator corresponding to the so called extended coupled cluster method (ECCM) [29] is obtained as follows

$$L_1 = L_0 - C_0 \tag{2.2.28a}$$

$$L_1' = L_1 - A_0 \tag{2.2.28b}$$

$$L_1'' = L_1' - D_0 \tag{2.2.28c}$$

$$L_k = L_{k-1}'' - C_{k-1} \tag{2.2.29a}$$

$$L_k' = L_k - A_{k-1} \tag{2.2.29b}$$

$$L_k'' = L_k' - D_{k-1} . \tag{2.2.29c}$$

The evolution **operator is** given by

$$U = \prod_{k=0} [\exp (W_k) \exp (Y_k) \exp (Z_k)];$$

$$W_k \in C_k,\ Y_k \in A_k,\ Z_k \in D_k . \tag{2.2.30}$$

The effect of **U** on the **vacuum** state is determined by three sets of parameters since

$$U|0\rangle = \exp [\sum_m S_{m0}\, a^{+m}] \exp [\sum_m y_{0m}\, a^{m}] \exp(S_{00})|0\rangle \tag{2.2.31}$$

The equations of motion for the different cluster amplitudes S [illegible] are obtained **from** eq.(2.2.10). When truncations are made in the operator set, these equations also contain finite order **polynomials only.**

Note that while the coefficients of the annihilation operator have no role to play in the **NCCM** approach, they influence the diagonal and higher rank cluster operators in the

ECCM. Thus the computational effort in the NCCM is roughly half of that required by ECCM. In general, if one is interested only in the calculation of correlation functions or scattering amplitudes, the NCCM is preferable. On the other hand if expectation values are desired, the ECCM becomes the preferred method. This can be seen from the expressions for expectation values by both approaches over an arbitrary initial state $|m\rangle$. Since $U^{+} = U^{-1}$, we get from eq(2.2.25) for NCCM

$$\langle m|U^{+}\ O\ U|m\rangle_{NCCM} = \langle m|\prod_{l=m}^{0} \exp(-Y_l) \prod_{k=\infty}^{0} (\exp(-Z_k) \exp(-W_k))\ O$$

$$\prod_{k=0}^{m} [\exp(W_k) \exp(Z_k)] \prod_{l=0}^{m} \exp(Y_l)\ |m\rangle . \quad (2.2.32)$$

The corresponding expression for ECCM is given by

$$\langle m|U^{+}\ O\ U|m\rangle_{ECCM} = \langle m|\prod_{k=m}^{0} [\exp(-Z_k) \exp(-Y_k) \exp(-W_k)]\ O \times$$

$$\prod_{k=0}^{m} [\exp(W_k) \exp(Y_k) \exp(Z_k)]\ |m\rangle .$$

(2.2.33)

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

2.2d. Generalizations to multidimensional systems.

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

$$H = \sum_{i\le j=1}^{D} p_i p_j /2m_{ij} + \sum_{i=1}^{D} V_i^{(1)} q_i + 1/2! \sum_{i,j=1}^{D} V_{ij}^{(2)} q_i q_j + \dots \qquad (2.2.34a)$$

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

$$L_0 = \{ \prod_{i=1}^{D} q_i^{n_i} p_i^{m_i} \;\; ; \; 0 \le n_i , m_i \le 1 \} \qquad (2.2.35a)$$

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

$$H = \sum_{m_i, n_i = 0}^{\infty} h(m_1 n_1 \; m_2 n_2 \dots\dots m_D n_D) \prod_{\alpha} a_\alpha^{+m_\alpha} a_\alpha^{n_\alpha} \qquad (2.2.34b)$$

$$L_0 = \{ \prod_{\alpha=1}^{D} a^{+m_\alpha} a^{n_\alpha} \; : \; 0 \leq m_\alpha, n_\alpha \leq \infty \}. \qquad (2.2.35b)$$

A sequence of subalgebras similar to the 1-d AHO algebra can be found here also and can be used to factorise the time evolution operator. For example, the multidimensional analogues of C_0, D_0 and L_1 are given by

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

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

$$L_1' = \{ \prod_{\alpha=1}^{D} a_\alpha^{+\,n_\alpha} a_\beta \; ; \quad 0 \leq n_\alpha \leq \infty \}. \qquad (2.2.36c)$$

With this, U can be parametrized as

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

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

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

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

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

$$U_1 = \exp[\sum_{\alpha} \sum_{n_1 n_2 ..} S^1_{n_1 n_2 ..;\alpha} (a_1^+)^{n_1} (a_2^+)^{n_2} ... a_\alpha] [\sum_{\alpha,\beta} U'_{\alpha\beta} a_\alpha^+ a_\beta]. \qquad (2.2.37d)$$

2.3. CONCLUDING REMARKS

Dynamics of initially prepared states on anharmonic surfaces play a fundamental role in many processes of chemical interest. Exponentially repulsive potentials are used to model the dynamics of photodissociation processes and inelastic molecular collisions. Morse functions are used to model highly anharmonic bond stretch motions. Double well functions are uaed to model potential surfaces on which reactive collisions take place. All these are examples of anharmonic potential energy surfaces [37].

Lie-algebraic approaches to quantum dynamics have attracted considerable attention in recent years primarily because of the advantages such a description has to offer in terms of the compact expressions it provides for the generators of the time evolution operators and the hierarchy of convenient and highly accurate approxiation it allows.

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

The algebra of anharmonic oscillators can be realized in two different forms. Adopting the boson ladder operator representation, we found that the resulting algebraic evolution operator is just the time dependent generalization [21] of the CCM wave operator. Realizing that the logarithm of the wave operator is an additively separable operator asymptotically, the CCM postulates an exponential wave operator for the vacuum states [28]

$$U_c = \exp(S) \tag{2.4.1}$$

and decomposes the cluster operator into one, two, three,...N-body excitation operators. Generalizing to the open-shell systems, the CCM posits [27]

$$U = U_C \, U_V \qquad (2.4.2)$$

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

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

$$U = \exp(-iHt), \qquad (2.4.3)$$

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

$$\underset{\varepsilon \to 0}{\mathrm{Lt}} \quad H_\varepsilon = H_A + H_B . \tag{2.4.4}$$

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

$$\underset{\varepsilon \to 0}{\mathrm{Lt}} \quad U = U_A \; U_B . \tag{2.4.5}$$

Since the sets of operators which act on the Hilbert spaces of the two subsystems commute with each other, and each is closed under commutation separately, they form closed subalgebras of the complete operator set acting on the direct product space of these two Hilbert spaces. Thus, they are decoupled from each other. Parametrizing U in a Wei-Norman product form as suggested in Sec.2.2b is equivalent to disentangling the excitation and deexcitation operators such that it is in a normally ordered form with respect to the harmonic oscillator basis set.

Lastly, we return to the choice of the basis vectors to the operator space. As mentioned earlier, the AHO operator space can be realized in the coordinate space as $L_0 = \{q \;\; p \;\; ; \; 0 \leq m, n < \infty \}$ where q and p are the coordinate and momentum operators respectively. The decoupling procedure discussed in Sec.2.2c is operative here also and L_0 can be factorised as

a. Sets of coordinate operators

$$C_k = \{ q^{(k+n)} \;\; p^k \;\; ; \;\; n \geq 1 \} \qquad 0 \leq k \leq \infty \tag{2.4.6a}$$

b. Sets of momentum operators

$$A_k = \{ q^k \; p^{(k+n)} \;\; ; \; n \geq 1 \} \qquad 0 \leq k \leq \infty \tag{2.4.6b}$$

c. Sets of diagonal operators

$$D_k = \{ q^k \;\; p^k \} \qquad 0 \leq k \leq \infty \tag{2.4.6c}$$

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

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

$$W_k \in C_k, \; Z_k \in D_k, \;\; Y_l \in A_l \tag{2.2.8}$$

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

where $m > k \geq 0$.

$$2)\ U = \prod_{k=0} [\exp(W_k) \exp(Y_k) \exp(Z_k)];$$

$$W_k \in C_k,\ Y_k \in A_k,\ Z_k \in D_k. \qquad \textbf{(2.2.9)}$$

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

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

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

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

REFERENCES

1. R. Kosloff, J. Phys. Chem., 92, 2087(1988).
2. (a) B. Gazdy and D.A. Micha, J. Chem. Phys., 82, 4926(1985).;(b) D.A. Micha Int. J. Quantum Chem.,23, 551(1983);(o) E.Vilallonga and D.A.Micha, Int.J.Quantum Chem Symp,15, 653(1981);(d) idem, J.Chem. Phys.,79, 3794(1983). (e). J Recamier, D.A. Micha and B. Gazdy, Chem. Phys. Lett., HO, 383 (1985); (f) J. Echave, F.M. Fernandez and D. A. Micha, J. Chem. Phys., 94, 3537 (1991); (g) J. A. Recamier, D.A. Micha and B. Gazdy, J. Chem. Phys., 85, 5093 (1986).
3. J. Kucar and H.D. Meyer, J. Chem. Phys., 90, 5566 (1989).
4. S. Shi and H.A. Rabitz, J. Chem. Phys.,92, 364(1990).
5. I. Benjamin, J. Chem. Phys., 85, 5611(1986).
6. a) H.K. Shin, Chem. Phys. Lett., 3, 125(1969);b) idem, J. Chem Phys. 81, 220 (1981).
7. Y. Alhassid and R. D. Levine, J. Chem. Phys., 67, 4321(1977).
8. J.Yuan and R. Gilmore, J. Chem. Phys., 86, 130(1987).
9. E. J. Heller, Acc. Chem. Res, 14, 386(1981).
10. D.J. Huber and E.J. Heller, J. Chem. Phys., 87, 5302(1987).
11. E. J. Heller, J. Chem. Phys., 94, 2723(1991)
12. D.J. Huber, S. Ling, D.G. Imre and E.J. Heller, J. Chem. Phys., 90, 7317(1989).
13. P.Pechukas and J.C.Light,J. Chem. Phys.,4.4, 3897(1966).
14. W.H.Miller, Adv. Chem. Phys.,25, 69(1974).
15. W.H.Miller ,Adv. Chem. Phys.,30, 77(1974).
16. W. Magnus, Commun. Pure. Appl. Math., 7, 649(1954).
17. R.M.Wilcox ,J. Math. Phys.,8, 962(1967).
18. J. Wei and E. Norman, J. Math. Phys., 4, 575(1963).

19. F. Wolf and H.J. Korsche, Phys. Rev. A, 37, 1934(1988)

20. G. Sree latha and M.Durga Prasad, Theor. Chim.Acta, 88, 511 (1993)

21. M. Durga Prasad, J. Chew. Phys.,88, 7005 (1988); Proc. Ind. Acad.Sci. (Cheat. Sci.),99, 61(1987) ; Lecture notes in chemistry Vol.50 edited by D.Mukherjee p321 (Springer, Berlin, 1989); S. Guha and D. Mukherjee, Chem. Phys. Lett., 186, 84(1991).

22. R.F. Bishop and H.G. Kummel, Physics Today, 40, 52(1987).

23. F. Coester, Nucl. Phys. 7, 421 (1958); F.Coester and H. Kummel, Nucl. Phys., 17, 477(1960).

24 J. Cizek, J. Chem. Phys., 45, 4256(1966); J. Cizek, Adv. Chem. Phys., 14, 35 (1969); R. J. Bartlett, J. Phys. Chem.,93, 1697 (1989).

25. D. Mukherjee, R. Moitra and A. Mukhopadhyay, Mol. Phys., 30, 1861(1975); idem, 33, 955(1977); D. Mukherjee, Int. J. Quantum Chem. 520, 409 (1986);Pramana,12, 203(1979).

26. I. Lindgren, Int. J. Quantum Chem. S12, 33 (1978); A. Haque and D. Mukherjee, J. Chem. Phys., 80, 5058(1984).

27. D. Mukherjee and S. Pal. Adv. Quantum Chem., ZO, 292(1989); I. Lindgren and D. Mukherjee , Phys. Rept., 151, 93(1987).

28. R. Chowdhary, D. Mukherjee and M. Durga Prasad, in Lecture notes in chemistry Vol.50 edited by D. Mukherjee p.3 (Springer, Berlin 1989).

29. J. Arponen, Ann. Phya., 151, 311 (1983); R.F. Bishop, J. Arponen and E. Pajanne, Lecture notes in chemistry Vol.50 edited by D. Mukherjee p.79 (Springer, Berlin 1989).

30. K. Emrich, Nucl. Phys. 4331, 379,397 (1981); H.J. Monkhorst, Int. J. Quantum Chem., S11, 421 (1977).

31. R.F. B shop and M.F. Flynn, Phys. Rev. A, 38, 2211 (1988).

32. C.S.Hsue and J.L. Chern, Phys. Rev. D, **29**, 643 (1984).

33. U.B. Kaulfuss and M. Altenbokum, Phys. Rev. D, 33, 3658 (1986).

34. R.F. Bishop, M.C. Bosca and M.F. Flynn, Phys. Rev. A, 40, 3484 (1989).

35. R. F. Bishop, M.C. Bosca and M.F. Flynn, Phys. Lett. A, **132**, 440 (1988).

36. J. Arponen, R.F. Bishop and E. Pajanne, Phys. Rev. A, 36, 2519, 2539 (1987).

37. R.D.Levine and R.B.Bernstein, *Molecular reaction Dynamics and Chemical Reactivity*, Ch.3,4, (Oxford University Press, Oxford, (1987)).

CHAPTER 3

APPLICATIONS TO ONE-DIMENSIONAL SYSTEMS: CONVERGENCE STUDIES

3-1. INTRODUCTION

To test the validity of the algebraic formalism presented in chapter 2. we will discuss a few model applications in this chapter. The stiffness of the non-linear equations, which are obtained in this formalism, has to be tested and simultaneously one would like to know how well the S-matrix elements converge with respect to the truncation index N. We study the application of this formalism to vacuum state propagation on one-dimensional potentials so that the results can be compared with the converged results from the linear basis set expansion method to test its accuracy. The hamiltonian for any one-dimensional system in general can be written as

$$H = p^2/2m + V \qquad (3.1.1)$$

where p is the momentum operator and V describes the potential energy surface. Obviously all the systems differ only in the form of the potential energy surface. The potentials we have chosen to study are

1) The exponentially repulsive potential,
2) The Morse potential,
3) Harmonic oscillator + time driven exponentially repulsive potential.

We will discuss the dynamics of these three systems in the next section and discuss the convergence of the S-matrix elements.

3.2. DYNAMICS ON THE EXPONENTIALLY REPULSIVE SURFACE.

The hamiltonian consisting of an exponentially repulsive potential and the kinetic energy operator is

$$H = p^2 / 2m + F \exp [-\alpha (q)] \tag{3.2.1}$$

where, F and α are constants. This hamiltonian models various processes of physical significance involving molecular collisions, photofragmentation processes, etc, and has been studied in great detail for these processes. Being a simple system we want to test our methodology on this system and then go to the more complicated ones. Converting this hamiltonian in terms of the harmonic oscillator ladder operators, we get

$$H = \hbar\omega /4 [2a^+a + 1 - a^{+2} - a^2] + F \exp [Z(a^+ + a)] \tag{3.2.2}$$

where,

$$Z = -\alpha \sqrt{(\hbar /2m\omega)}. \tag{3.2.3}$$

As the potentials used in this chapter are transcendental functions, we explicitly derive the working equations in detail to show that the derivation of these equations though tedious is

relatively straightforward and involves no further approximations.

3. 2a. Working Equations.

The equations of motion are obtained by solving the time dependent Schroedinger equation given by

$$i U = H U. \qquad (3.2.4)$$

As we are interested in calculating the autocorrelation and the transition probabilities from the ground to the higher eigenstates of the harmonic oscillator number operator which require only the ground state propagation, the evolution operator given by eq. (2.2.25) in chapter 2, reduces to

$$U_0 \mid 0 > = \exp [\Sigma S_m a^{+m}] \mid 0 > \qquad \mathbf{(3.2.5)}$$

premultiplying eq. (3.2.5) with U we obtain

$$i U^{-1} \dot{U} = U^{-1} H U \qquad \mathbf{(3.2.6)}$$

which we solve to obtain the desired properties. Substituting eq (3.2.5) in the above equation we obtain

$$i \exp [-\Sigma S_m a^{+m}] \, d/dt \exp [\Sigma S_m a^{+m}] = \exp [-\Sigma S_m a^{+m}]$$

$$H \exp [\Sigma S_m a^{+m}]. \qquad \mathbf{(3.2.7)}$$

We will first consider the left hand side (L.H.S.) of the above equation

$$\text{L.H.S.} = i \exp [-\sum_n S_n a^{+n}] \, d/dt \, \exp [\sum_n S_n a^{+n}]$$

$$= i \{ d/dt + [d/dt, \sum_n S_n a^{+n}]$$

$$+ 1/2! \, [[d/dt, \sum_n S_n a^{+n}], \sum_m S_m a^{+m}] + \ldots\ldots \}$$

$$= i \{ d/dt + \sum_n \dot{S}_n a^{+n} + 0 + 0 + \ldots\ldots \}. \qquad \textbf{(3.2.8)}$$

Here the second line follows from the well known Hausdorff expansion [1] and the observation that all creation operators commute with each other.

We next turn to the right hand side (R.H.S.) of eq(3.2.7)

$$\text{R.H.S.} = \exp [-\sum_n S_n a^{+n}] \, H \, \exp [\sum_n S_n a^{+n}]$$

$$= \exp [-\sum_n S_n a^{+n}] \{\hbar\omega/4 \; (2a^+a + 1 - a^{+2} - a^2) \exp [\sum_n S_n a^{+n}]\}$$

$$+ \exp [-\sum_n S_n a^{+n}] \, F(t) \exp[Z(a^+ + a)] \exp [\sum_n S_n a^{+n}]. \quad (3.2.9)$$

Consider the first term in eq. (3.2.9). This gives by Hausdorff expansion

$$\exp\,[-\sum_n S_n\, a^{+n}\,]\;\hbar\omega/2\;(a^{+}a\;)\;\exp\,[\sum_n S_n\, a^{+n}\,]$$

$$= \hbar\omega\,/2\;\{\;a^{+}a + [\;a^{+}a,\;\sum_n S_n\, a^{+n}\,]$$

$$+1/2!\;[[a^{+}a,\sum_n S_n\, a^{+n}\,],\;\sum_m S_m a^{+m}\,]\;+\ldots.\}$$

$$= \hbar\omega\,/2\;\{\;a^{+}a + \sum_n n\;S_n\;a^{+n}\,\}, \qquad (3.2.10)$$

Here again, the last line follows because the creation operators commute with each other.

The second term in eq. (3.2.9) is given by

$$U^{-1}\;[\hbar\omega/4\;]\;U = \hbar\omega\;/4\,. \qquad (3.2.11)$$

Similarly, the third term in eq. (3.2.9) is given by

$$U^{-1}\;[\;-\hbar\omega/4\;a^{+2}\;]\;U = -\hbar\omega/4\;a^{+2}. \qquad (3.2.12)$$

We now evaluate the fourth term in the expansion given by eq. (3.2.9)

$$U^{-1}\;[\;-\hbar\omega\;/4\;a^{2}\;]\;U = \quad \exp\,[-\sum_n S_n\;a^{+n}\,]\;\;[-\hbar\omega/4\;a^{2}]\;\;\exp\,[\sum_n S_n\;a^{+n}\,]$$

$$= -\hbar\omega\;/4\;\{\;a^{2} + [\;a^{2},\;\sum_n S_n\;a^{+n}\,]$$

$$+1/2!\;[[a^{2}\;,\sum_n S_n\;a^{+n}\,],\;\sum_m S_m a^{+m}\,]\;+\ldots.\}$$

$$= -\hbar\omega/4\ a^2 - \hbar\omega/4 \sum S_n\ [\ 2na^{+(n-1)}a\ ]$$

$$-\hbar\omega/4 \sum S_n\ n\ (n-1)\ a^{+(n-2)}$$

$$- \hbar\omega/8 \sum_{n,m} S_n\ S_n\ 2nm\ a^{+\ (n+m-2)}. \qquad \mathbf{(3.2.13)}$$

Turning to the remaining term in **eq.(3.2.9)** we first express exp [Z (a + a)] in normal order [1]

$$\exp\ [Z\ (a^+ + a)] = \exp\ (Za^+)\ \exp(Za)\ \exp\ (Z^2/2). \qquad \mathbf{(3.2.14)}$$

With this and using the resolution of identity in the form $\exp\ (-Za)\ \exp\ (Za) = 1$, we obtain

$$\exp\ [-\sum_n S_n\ a^{+n}\ ]\ F\ \exp\ [Z(a^+ + a)]\ \exp\ [\sum_n S_n\ a^{+n}]$$

$$= F\ \exp\ (Z^2/2)\ \exp\ [-\sum_n S_n\ a^{+n}\ ]\ \exp\ (Za^+)\ \exp(Za)$$

$$\times \qquad \exp[\sum_n S_n\ a^{+n}\ ]\ \exp(-Za)\ \exp(Za)$$

$$= F\ \exp\ (Z^2/2)\ \exp(Za^+)\ \exp\ [-\sum_n S_n\ a^{+n}\ ]\ \{\ \exp(Za)$$

$$\times \qquad \exp[\sum_n S_n\ a^{+n}\ ]\ \exp(-Za)\ \}\ \exp\ (Za). \qquad \mathbf{(3.2.15)}$$

Here the second line **follows** because Za and S commute with each other. To continue further we expand the term in the braces by Hausdorff expansion and obtain

$$=F \exp(Z^2/2) \exp(Za^+) \quad \exp[-\sum_n S_n a^{+n}] \; \{\sum_{k=0} 1/k! \exp(Za)$$

$$X \qquad \{\sum_n S_n a^{+n}]^k \exp(-Za)\} \exp(Za)$$

$$=F \exp(Z^2/2) \exp(Za^+) \quad \exp[-\sum_n S_n a^{+n}]$$

$$X \qquad \{\sum_{k=0} 1/k! \, [\exp(Za) \sum_n S_n a^{+n} \; \exp(-Za)]^k \}\exp(Za)$$

$$=F \exp(Z^2/2) \exp(Za^+) \quad \exp[-\sum_n S_n a^{+n}]$$

$$X \qquad \exp\{\exp(Za) \, [\sum_n S_n a^{+n}] \exp(-Za)\} \exp(Za)$$

$$=F \exp(Z^2/2) \exp(Za^+) \quad \exp[-\sum_n S_n a^{+n}]$$

$$X \exp\{\sum_n S_n \{a^{+n} + [Za, a^{+n}] + 1/2! \, [Za, [Za, a^{+n}]] + \ldots\}\} \exp(Za)$$

$$=F \exp(Z^2/2) \exp(Za^+) \quad \exp[-\sum_n S_n a^{+n}]$$

$$X \exp[\sum_n S_n \{a^{+n} + Zna^{+n-1} + 1/2! \, n(n-1) Z^2 a^{+n-2} + ..\}] \exp(Za)$$

$$=F \exp(Z^2/2) \exp(Za^+) \quad \exp[-\sum_n S_n a^{+n}]$$

$$X \quad \exp[\sum_n S_n \{\sum_{r=0}^{n} {}^nC_r \, Z^r a^{+n-r}\}] \exp(Za). \qquad (3.2.16)$$

Given that a^{+}, a^{+n}, a^{+n-r} all commute, we can combine the first three exponential operators in the above expression and write

$$=F \exp(Z^2/2) \exp\left[Za^{+} - \sum_{n} S_n a^{+n} + \sum_{n} S_n \left\{ \sum_{r=0}^{n} {}^{n}C_r Z^r a^{+n-r} \right\}\right]$$

$$X \quad \exp(Za). \qquad (3.2.17)$$

Further, separating r=0 term,

$$=F \exp(Z^2/2) \exp\left[Za^{+} - \sum_{n} S_n a^{+n} + \sum_{n} S_n a^{+n} + \sum_{n} S_n \left\{ \sum_{r=1}^{n} {}^{n}C_r Z^r a^{+n-r} \right\}\right]$$

$$X \exp(Za)$$

$$=F \exp(Z^2/2) \exp\left[Za^{+} + \sum_{n} S_n \left\{ \sum_{r=1}^{n} {}^{n}C_r Z^r a^{+n-r} \right\}\right]$$

$$X \quad \exp(Za)$$

$$=F \exp(Z^2/2) \exp\left[Za^{+} + \sum_{n=1} S_n Z^n + \sum_{n} S_n \left\{ \sum_{r=1}^{n-1} {}^{n}C_r Z^r a^{+n-r} \right\}\right]$$

$$X \quad \exp(Za)$$

$$=F \exp\left(Z^2/2 + \sum_{n=1} S_n Z^n\right) \exp\left[Za^{+} + \sum_{n} S_n \left\{ \sum_{r=1}^{n-1} {}^{n}C_r Z^r a^{+n-r} \right\}\right]$$

$$X \quad \exp(Za). \qquad (3.2.18)$$

Defining a new index s via a = n-r and eliminating r in eq. (3.2.18) gives us

$$=F \exp\left(Z^2/2 + \sum_{n=1} S_n Z^n\right) \exp\left[Za^+ + \sum_n S_n \left\{ \sum_{s=1}^{n-1} {}^nC_{n-s} Z^{n-s} a^{+s} \right\}\right]$$

$$\times \quad \exp(Za)$$

$$=F \exp\left(Z^2/2 + \sum_{n=1} S_n Z^n\right) \exp\left[Za^+ + \sum_{s=1} a^{+s} \left\{ \sum_{n=s+1} S_n {}^nC_{n-s} Z^{n-s} \right\}\right]$$

$$\times \quad \exp(Za). \qquad (3.2.19)$$

We now define the following intermediate variables

$$Y_0 = F \exp\left(Z^2/2 + \sum_n S_n Z^n\right) \qquad (3.2.20a)$$

$$Y_1 = Z + \sum_{n=2} S_n {}^nC_{n-1} Z^{n-2} \qquad (3.2.20b)$$

$$Y_2 = \sum_{n=3} S_n {}^nC_{n-2} Z^{n-2} \qquad (3.2.20c)$$

$$Y_s = \sum_{n=s+1} S_n {}^nC_{n-s} Z^{n-s} \qquad s \geq 3 . \qquad (3.2.20d)$$

In terms of these equations, eq. (3.2.20) becomes

$$= Y_0 \exp(Y_1 a^+ + Y_2 a^{+2} + Y_3 a^{+3} + \dots) \exp(Za). \qquad (3.2.21)$$

Combining the expressions (3.2.21) and (3.2.13) for the right hand side of the Schroedingers equation along with eq.(3.2.8) for the left hand side we obtain,

$$i \sum \dot{S}_n a^{+n} = \hbar\omega/4 - \hbar\omega/4\, a^{+2} - \hbar\omega/4 \sum S_n\, n\,(n-1)\, a^{+(n-2)}$$

$$- \hbar\omega/8 \sum_{n,m} S_n S_n\, 2nm\, a^{+(n+m-2)} + Y_0 \exp [\sum Y_s a^{+s}]. \qquad (3.2.22)$$

We now note that since the operator a acting on vacuum state gives zero, a a operator does not contribute to the time evolution of that state. Similarly, exp(Za) on the right would not have any effect. To obtain explicit equations for S we have to expand the exponential in eq.(3.2.22). Thus,

$$i \sum \dot{S}_n a^{+n} = \hbar\omega/4 - \hbar\omega/4\, a^{+2} - \hbar\omega/4 \sum S_n\, n\,(n-1)\, a^{+(n-2)}$$

$$- \hbar\omega/8 \sum_{n,m} S_n S_n\, 2nm\, a^{+(n+m-2)}$$

$$+ Y_0 [1 + Y_1 a^{+} + Y_2 a^{+2} + Y_3 a^{+3} + \ldots.$$

$$+ Y_1^2 a^{+2}/2! + Y_1 Y_2 a^{+3} + \ldots\ldots + Y_1^3 a^{+3}/3! + \ldots\ldots\ldots]. \qquad (3.2.23)$$

Comparing the coefficients of a^{+n} on either side, we obtain the working equations of motion. We note that this requires no **approximations** or special mathematical techniques other than the **Hausdorff** expansion. The working equations of motion are given by

$$i\dot{S}_0 = -\hbar\omega/4 - \hbar\omega/2\ S_2 - \hbar\omega/4\ S_1^2 + Y_0 \qquad (3.2.24a)$$

$$i\dot{S}_1 = -3\hbar\omega/2\ S_3 + \hbar\omega/2\ S_1 - \hbar\omega\ S_1S_2 + Y_0Y_1 \qquad (3.2.24b)$$

$$i\dot{S}_2 = -3\hbar\omega\ S_4 + \hbar\omega/2\ S_1 - 3\hbar\omega/2\ S_1S_3 - 2\hbar\omega\ S_2^2 + \hbar\omega\ S_2$$

$$+ Y_0\ [Y_1^2/2! + Y_2\ ] \qquad (3.2.24c)$$

and the rest of the equations can be obtained similarly. The auto - correlation function A(t) is given by

$$A(t) = \langle 0\ |U\ |\ 0\rangle \qquad (3.2.25a)$$

$$= \exp\ [\ S_0\ ]. \qquad (3.2.25b)$$

3.2b. Numerical Studies:

We have carried out calculations for three different values of α= 0.025, 0.05, 0.1 and F= 1. In our calculations we have used the units in which $\hbar$ = 1. Tables 3.2.1a, 3.2.1b, 3.2.1c show the convergence of the S-matrix elements with respect to the truncation index N for the three different values of α after propagating the wave packet for ten time units. The values of the S-matrix elements converged very well. Although the values of the S-matrix elements at higher truncation indices are not identical, they are extremely small and do not contribute much in evaluating

TABLE 3.2.1a

S -matrix elements for the exponentially repulsive potential after 10 time units with $\alpha = 0.025$.

S_n N	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	-0.1078e+0 -0.1045e+3	0.3211e+0 (a) -0.1004e+0 (b)						
2	-0.3013e+1 -0.1066e+3	0.7364e-1 0.1975e+1	0.4948e+0 0.2687e-1					
3	-0.3018e+1 -0.1067e+3	0.7743e-1 0.1992e+1	0.4943e+0 0.2407e-1	0.8379e-5 0.2341e-3				
4	-0.3018e+1 -0.1067e+3	0.7761e-1 0.1993e+1	0.4942e+0 0.2386e-1	0.1616e-4 0.2623e-3	-0.2593e-6 -0.2159e-5			
5	-0.3018e+1 -0.1067e+3	0.7761e-1 0.1993e+1	0.4942e+0 0.2384e-1	0.1706e-4 0.2645e-3	-0.3672e-6 -0.2411e-5	0.5456e-8 0.1948e-7		
6	-0.3018e+1 -0.1067e+3	0.7761e-1 0.1993e+1	0.4942e+0 0.2384e-1	0.1713e-4 0.2646e-3	-0.3801e-6 -0.2432e-5	0.6970e-8 0.2169e-7	-0.9416e-10 -0.1830e-9	
7	-0.3018e+1 -0.1067e+3	0.7761e-1 0.1993e+1	0.4942e+0 0.2384e-1	0.1713e-4 0.2646e-3	-0.3812e-6 -0.2434e-5	0.7153e-8 0.2188e-7	-0.1154e-9 -0.2028e-9	0.1483e-11 0.1817e-11

(a) real part of the S -matrix elements.

(b) imaginary part of the S -matrix elements.

TABLE 3.2.1b

S -matrix elements for the exponentially repulsive potential after 10 time units with $\alpha = 0.05$.

S_n N	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	-0.1061e+0 -0.5140e+2	0.2298e+0(a) -0.3283e+0(b)						
2	-0.2665e+1 -0.5357e+2	0.1461e+0 0.1966e+1	0.4797e+0 0.5191e-1					
3	-0.2669e+1 -0.5359e+2	0.1531e+0 0.1979e+1	0.4776e+0 0.4679e-1	0.6589e-4 0.8903e-3				
4	-0.2669e+1 -0.5359e+2	0.1534e+0 0.1980e+1	0.4773e+0 0.4647e-1	0.1226e-3 0.9851e-3	-0.3812e-5 -0.1560e-4			
5	-0.2669e+1 -0.5359e+2	0.1534e+0 0.1980e+1	0.4773e+0 0.4645e-1	0.1284e-3 0.9908e-3	-0.5280e-5 -0.1701e-4	0.1516e-6 0.2512e-6		
6	-0.2669e+1 -0.5359e+2	0.1534e+0 0.1980e+1	0.4773e+0 0.4645e-1	0.1289e-3 0.9912e-3	-0.5432e-5 -0.1709e-4	0.1890e-6 0.2666e-6	-0.4858e-8 -0.3621e-8	
7	-0.2669e+1 -0.5359e+2	0.1534e+0 0.1980e+1	0.4773e+0 0.4645e-1	0.1289e-3 0.9912e-3	-0.5446e-5 -0.1709e-4	0.1929e-6 0.2669e-6	-0.5769e-8 -0.3613e-8	0.1372e-9 0.3522e-10

(a) real part of the S -matrix elements.

(b) imaginary part of the S -matrix elements.

TABLE 3.2.1c

S -matrix elements for the exponentially repulsive potential after 10 time units with $\alpha = 0.1$.

S_n N	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	-0.2789e+0 -0.4848e+2	0.3369e+0 (a) -0.5842e+0 (b)						
2	-0.1725e+2 -0.6181e+2	0.2502e+1 0.4644e+1	0.3799e+0 -0.7719e-1					
3	-0.1829e+2 -0.5859e+2	0.3104e+1 0.3464e+1	0.2660e+0 0.6042e-1	0.5765e-2 -0.4331e-2				
4	-0.1760e+2 -0.5858e+2	0.2726e+1 0.3463e+1	0.3443e+0 0.5789e-1	-0.1820e-2 -0.3753e-2	0.3218e-3 0.8232e-5			
5	-0.1764e+2 -0.5874e+2	0.2768e+1 0.3581e+1	0.3289e+0 0.2229e-1	0.1051e-2 0.1932e-2	0.4536e-4 -0.5157e-3	0.1148e-4 0.2734e-4		
6	-0.1769e+2 -0.5871e+2	0.2808e+1 0.3547e+1	0.3138e+0 0.3878e-1	0.4145e-2 -0.2369e-2	-0.3255e-3 0.1606e-3	0.3717e-4 -0.3699e-4	-0.7695e-6 0.3091e-5	
7	-0.1767e+2 -0.5870e+2	0.2789e+1 0.3536e+1	0.3245e+0 0.4241e-1	0.7757e-3 -0.2859e-2	0.3220e-3 0.1256e-3	-0.3979e-4 -0.1539e-4	0.4528e-5 0.1179e-6	-0.1715e-6 0.1231e-6

(a) real part of the S -matrix elements.

(b) imaginary part of the S -matrix elements.

the dynamics of the systems. Convergence is good for a = 0.025 and 0.05, but not so good for α = 0.1. For large values of α, the potential becomes steeper resulting in greater anharmonic effects in the system, These effects cause the wave packet to dephase at a faster rate. Consequently, the convergence pattern seen for large values of a is slower than for smaller values of a.

The transition probabilities P for the transition from the ground to the nth eigenstate of the hamiltonian as a function of time are plotted in Fig. 3.2.1a, 3.2.1b and 3.2.1c for different values of α and compared with the basis set expansion method. The equation to obtain the transition probabilities in the algabraic formalism is given by

$$P_n = |\langle n| \; U_0 \; |0\rangle|^2. \tag{3.2.26}$$

These are evaluated by substituting for U_0 from eq. (3.2.5)

$$P_n = |\langle n|\exp \left[\sum_{k=1}^{N} a^{+k} S_k + S_0 \right] |0\rangle|^2. \tag{3.2.27}$$

For example the values of P for the first three transitions are evaluated to be

$$P_1 = |e^{S_0} [S_1]|^2 \tag{3.2.28a}$$

$$P_2 = |e^{S_0} [S_1^2/2! + S_2]|^2 \tag{3.2.28b}$$

$$P_3 = |e^{S_0} [S_1^3/3! + S_1 S_2 + S_3]|^2. \tag{3.2.28c}$$

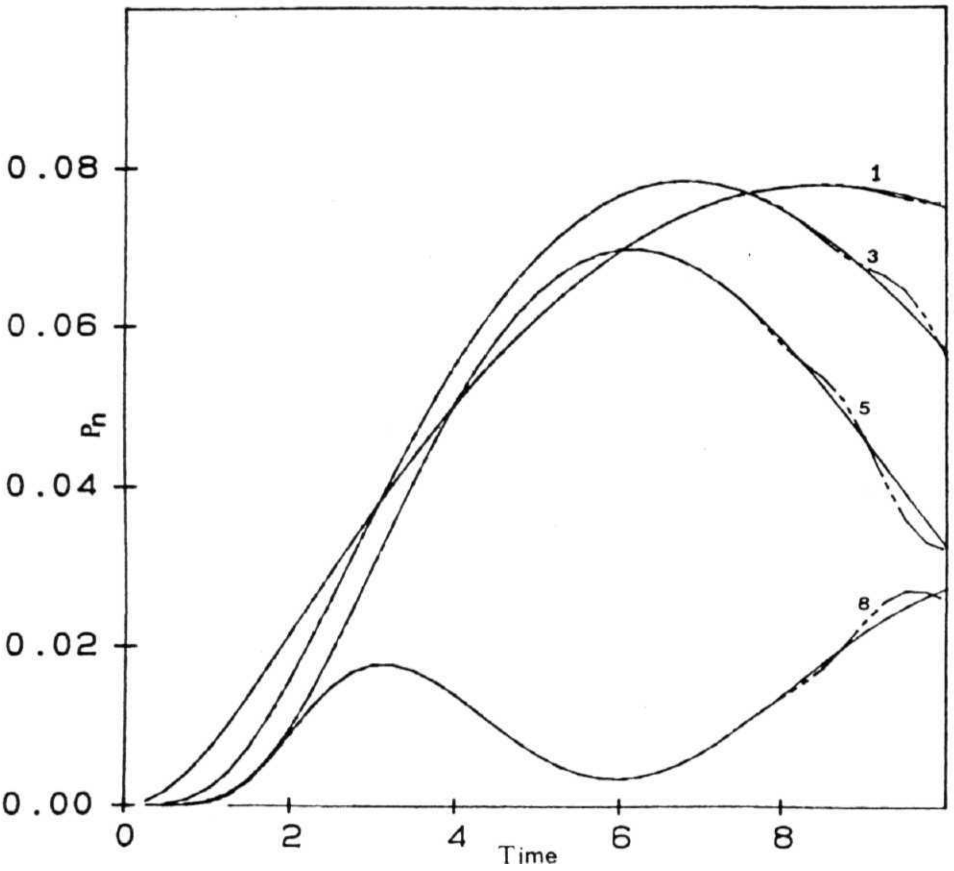


Fig. 3.2.1a: The transition probabilities P_n for n = 8, 5, 3 and 1 which are marked above each curve, as a function of time for α = 0.025 for the exponentially repulsive surface. Dash and double dot - basis set expansion and solid line - TDCCM at the truncation index N = 7.

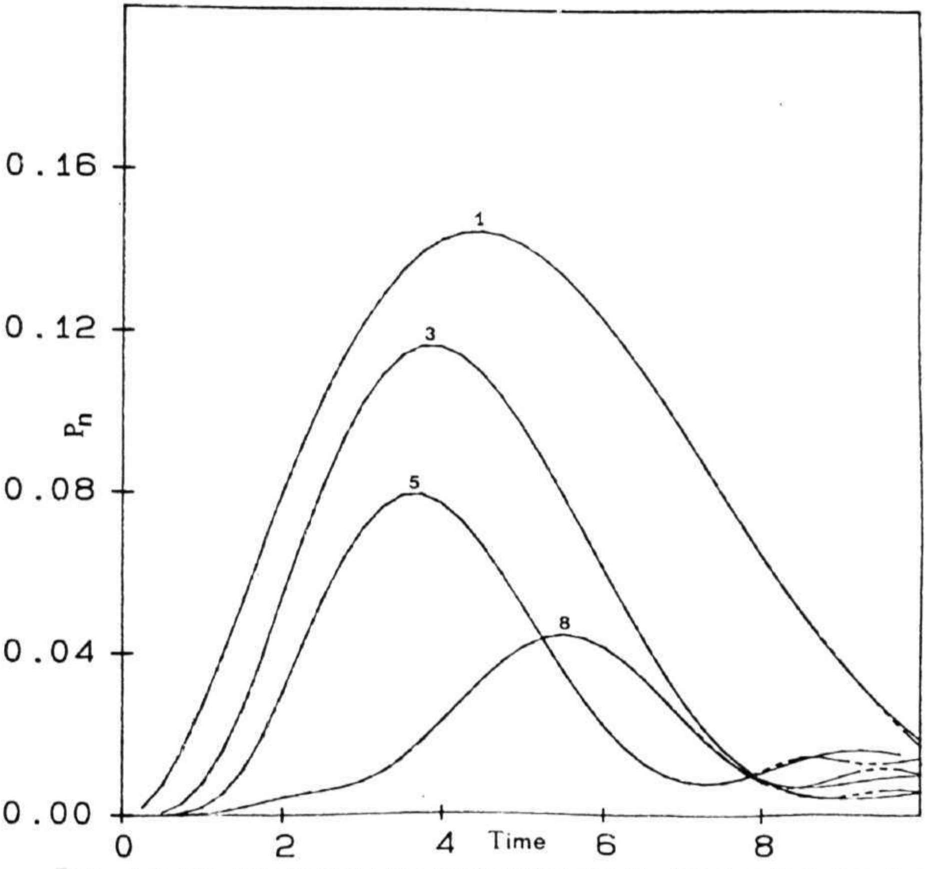


Fig. 3.2.1b: The transition probabilities P_n for n = 8, 5, 3 and 1 which are marked above each curve, as a function of time for α = 0.05 for the exponentially repulsive surface. Dash and double dot - basis set expansion and solid line - TDCCM at the truncation index N = 7.

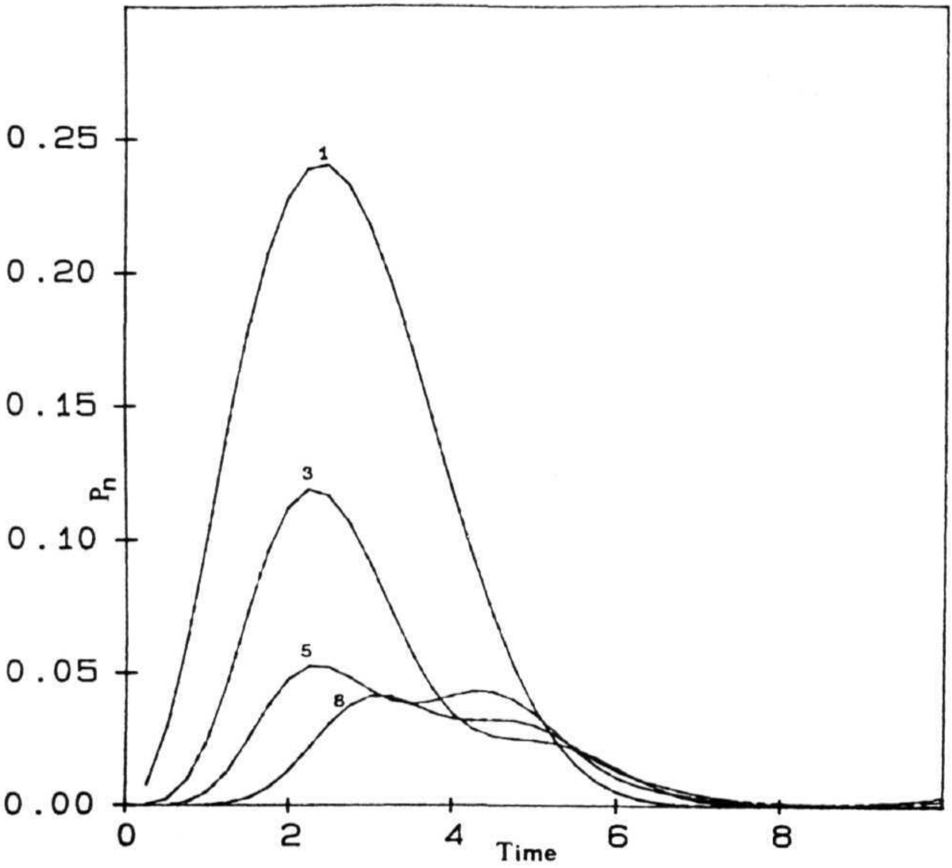


Fig. 3.2.1c: The transition probabilities P for n = 8, 5, 3 and 1 which are marked above each curve, as a function of time for α = 0.1 for the exponentially repulsive surface. Dash and double dot - basis set expansion and solid line - TDCCM at the truncation index N = 7.

Good agreement between the values obtained by the two approaches is seen. Nearing ten time units both the approaches do not tally as is seen from the figures. We attribute this to the nonconvergence of the basis set expansion approach which required large basis of about 120 functions. Due to lack of computational power we could not carry out the basis set calculations untill convergence.

Figures 3.2.2a , 3.2.2b and 3.2.2c show the comparison of the modulus of the autocorrelation function plotted against time obtained from the algebraic theory at $N = 7$ with the linear basis set expansion method for different values of α. For carrying out calculations for longer times, the basis set expansion approach requires a still larger basis for convergence. Good agreement with the exact results is seen.

The modulus of the converged autocorrelation function obtained from the algebraic theory for longer times is shown in Fig. 3.2.3a, 3.2.3b and 3.2.3c for $a = 0.025$,0.05 and 0.1 respectively with the truncation index $N=7$. This is to show that the converged algebraic calculations could be easily carried out for longer times with as few as 7 equations in contrast to the basis set expansion method.

In all these calculations the algebraic approach led to a faster convergence pattern than the basis set expansion approach. Also the working equations of motion in the algebraic approach were no more stiffer than the exact approach.

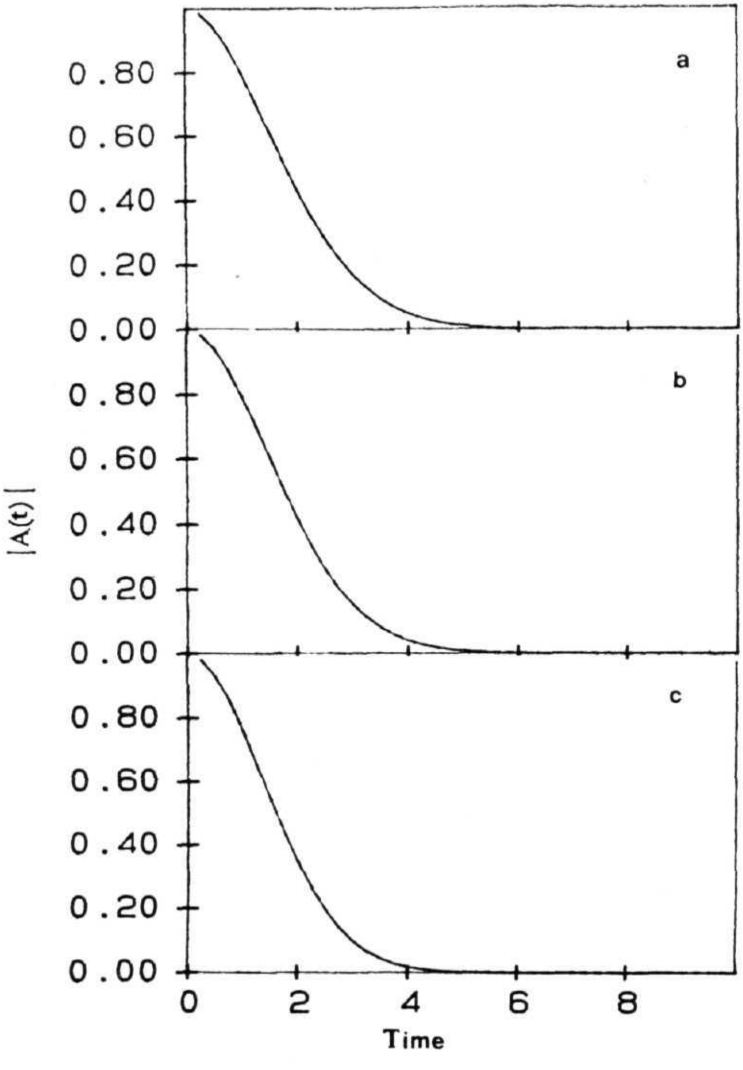


Fig. 3.2.2: Plots of the modulus of the autocorrelation function vs. time for the exponentially repulsive surface for different values of α. a) $\alpha = 0.025$, b) $\alpha = 0.05$ and c) $\alpha = 0.1$. Solid line - basis set expansion and dash and double dot - TDCCM at the truncation index N = 7.

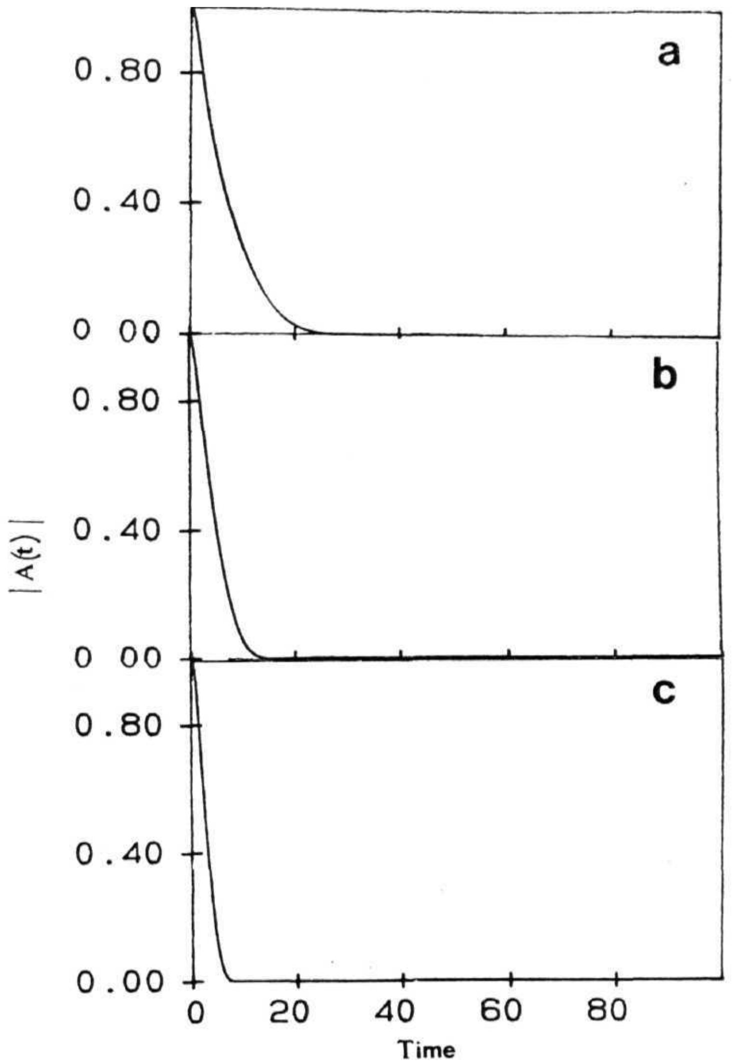


Fig. 3.2.3: Plots of the Modulus of the converged of the autocorrelation function vs. time obtained from TDCCH at the truncation index N = 7 for different values of α. a) α = 0.025, b) α = 0.05 and c) α = 0.1.

3.3. DYNAMICS ON THE MORSE POTENTIAL ENERGY SURFACE.

As a second example, we studied the dynamics of gaussian states on a displaced Morse potential [2-6]. The Morse potential is a good approximation to the potential of diatomic molecules and has been the standard test potential for several dynamical studies [2]. The hamiltonian of this system is given by

$$H = (p - p_0)^2/2m + D\,[\,1 - \exp(-\alpha\,(q-q_0))]^2 \qquad (3.3.1)$$

where D is the depth of the potential energy minimum and hence represents the dissociation energy of the system, p_0 and q are the initial momentum and initial position of the wave packet respectively. a is given by the equation

$$\alpha = \mathrm{sqrt}\,(\,\mu\,/2D)\,\omega \qquad (3.3.2)$$

μ is the reduced mass of the system and ω is the harmonic frequency. The spectroscopist's anharmonic constant x is related to the parameters occuring in eq. (3.3.1) by

$$x_e = \omega\,/\,4D\,. \qquad (3.3.3)$$

The number of bound states n is given by

$$n = 2D/\hbar\omega - 1/2\,. \qquad (3.3.4)$$

3.3a. Working Equations.

Our next attempt is to perform convergence studies on the system. The equations of motion are obtained by solving the time dependent Schroedinger equation given by eq. (3.2.4). The corresponding evolution operator is given by eq. (3.2.5). The methodology is identical to the one decribed for the exponentially repulsive potential surface described in Sec. 3.2a. Converting the hamiltonian in terms of the harmonic oscillator ladder operators and substituting the expression for the time evolution operator in the TDSE for the R.H.S. we obtain

$$U^{-1} H U = U^{-1} \hbar\omega /4 \; [\, 2a^{+}a + 1 - a^{+2} - a^{2}] + Z\,(a^{+} - a) + p_0^{2}/2\mu + D \exp [Z_1(a^{+} + a)] - 2D \exp [Z_2(a^{+} + a)] \tag{3.3.5}$$

where,

$$Z = -2p_0 \sqrt{(\mu\omega/\hbar)}\, i \tag{3.3.6}$$

$$Z_1 = -2\alpha \sqrt{(\hbar/2\mu\omega)} \tag{3.3.7}$$

and

$$Z_2 = 2\, Z_1 . \tag{3.3.8}$$

The evaluation of the first term in the equation (3.3.5) is similar to that discussed in Sec. 3.2a. The second term in the hamiltonian contains linear terms in a and a . As a commutes with U the multicommutator Hausdorff expansion gives only Za the rest being equal to zero. The operator a gives

$$U^{-1}\ a\ U = a + \Sigma\ S_n\ n\ a^{+(n-1)}. \qquad (3.3.9)$$

The third term being a constant again commutes with S to give

$$U^{-1}\ p_0^2/2\mu\ U = p_0^2/2\mu. \qquad (3.3.10)$$

The fourth term can be split into three terms as

$$U^{-1}\ D\ [\ 1 - \exp\ (-\alpha\ (q-q_0))]^2\ U = U^{-1}D\ U + U^{-1}\ D\ \exp\ [Z_1(a^+ + a)]\ U$$

$$- U^{-1}\ 2D\ \exp\ [Z_2(a^+ + a)]\ U. \qquad (3.3.11)$$

Each term in the above equation is expanded as the Hausdorff expansion. From the first term we obtain

$$U^{-1}\ D\ U = D. \qquad (3.3.12)$$

The second term in eq. (3.3.11) can be obtained similar to the derivation for the exponentially repulsive surface

$$U^{-1}\ D\ \exp\ [Z_1(a^+ + a)]\ U = R_0\ [1 + R_1 a^+ + R_2 a^{+2} + R_3 a^{+3} + \ldots.$$

$$+ R_1^2 a^{+2}/2! \quad + R_1 R_2 a^{+3} + \ldots.. + R_1^3 a^{+3}/3! + \ldots\ldots\ldots]. \qquad (3.3.13)$$

The expressions for **R** (r ≥ 1) are identical to those of **Y** in Sec.

3.2a given by the **eq.** (3.2.20), except that F and Z are replaced by D and Z **respectively**. The third term in **eq.** (3.3.11) is expanded using the Hausdorff expansion as

$$U\ \{-2D \exp [Z_2(a^{+} + a)]\}\ U = X_0\ [1 + X_1 a^{+} + X_2 a^{+2} + X_3 a^{+3} + \ldots.$$
$$+ X_1^2 a^{+2}/2! \ + X_1 X_2 a^{+3} + \ldots.. + X_1^3 a^{+3}/3! + \ldots\ldots\ldots].$$

(3.3.14)

Here the equations for X are again identical to the equations for Y_r given by equations (3.2.20) except that F and Z are replaced by -2D and Z_2 **respectively**. The L.H.S. of the TDSE is given by **eq.** (3.2.8). The complete equation after **all** the expansions are done is now given by

$$i \sum \dot{S}_n\ a^{+n} = \hbar\omega/4 - \hbar\omega/4\ a^{+2} \ -\hbar\omega/4 \sum S_n\ n\ (n-1)\ a^{+(n-2)}$$

$$- \hbar\omega/8 \sum_{n,m} S_n\ S_n\ 2nm\ a^{+\ (n+m-2)} + \sum S_n\ n\ a^{+(n-1)}$$

$$+ Z\ a^{+} + p_0^2/2\mu + \ R_0\ [1 + R_1 a^{+} + R_2 a^{+2} + R_3 a^{+3} + \ldots.$$

$$+ R_1^2 a^{+2}/2! \ + R_1 R_2 a^{+3} + \ldots.. + R_1^3 a^{+3}/3! + \ldots\ldots\ldots]$$

$$+ \ X_0\ [1 + X_1 a^{+} + X_2 a^{+2} + X_3 a^{+3} + \ldots.$$

$$+ X_1^2 a^{+2}/2! \ + X_1 X_2 a^{+3} + \ldots.. + X_1^3 a^{+3}/3! + \ldots\ldots\ldots]$$

(3.3.15)

TABLE 3.3.1a

S -matrix elements for the Morse potential after 10 time units with $q_0 = -13.45$.

S_n N	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	-0.1616e+1 -0.9348e+2	-0.3183e+0 (a) 0.3320e+0 (b)						
2	-0.1856e+1 -0.9429e+2	0.1647e+0 -0.1141e+1	0.4403e+0 0.2032e+0					
3	-0.1780e+1 -0.9431e+2	0.1959e+0 -0.1167e+1	0.4485e+0 0.1864e+0	0.3620e-2 -0.4583e-2				
4	-0.1786e+1 -0.9431e+2	0.1911e+0 -0.1168e+1	0.4469e+0 0.1865e+0	0.3121e-2 -0.4285e-2	-0.1528e-3 0.5627e-4			
5	-0.1786e+1 -0.9431e+2	0.1908e+0 -0.1168e+1	0.4468e+0 0.1866e+0	0.3085e-2 -0.4251e-2	-0.1572e-3 0.7255e-4	-0.2342e-5 0.4548e-5		
6	-0.1786e+1 -0.9431e+2	0.1908e+0 -0.1168e+1	0.4468e+0 0.1867e+0	0.3112e-2 -0.4223e-2	-0.1488e-3 0.7316e-4	0.1636e-6 0.3352e-5	0.7575e-6 0.2721e-7	
7	-0.1786e+1 -0.9431e+2	0.1909e+0 -0.1168e+1	0.4468e+0 0.1866e+0	0.3117e-2 -0.4235e-2	-0.1491e-3 0.7720e-4	0.2985e-6 0.4219e-5	0.5874e-6 -0.1198e-6	-0.4124e-7 -0.4803e-7

(a) real part of the S -matrix elements.

(b) imaginary part of the S -matrix elements.

TABLE 3.3.1b

S -matrix elements for the Morse potential after 10 time units with $q_0 = -5.56$.

S_n N	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	-0.4122e+1 -0.3255e+2	-0.1650e+1 (a) 0.1493e+1 (b)						
2	-0.7366e+1 -0.6906e+2	0.9936e+0 -0.3036e+1	0.3679e+0 0.3337e+0					
3	-0.8805e+1 -0.7066e+2	0.7419e+0 -0.3459e+1	0.3364e+0 0.2617e+0	-0.1335e-2 -0.1138e-1				
4	-0.7210e+1 -0.6987e+2	0.1099e+1 -0.3178e+1	0.3878e+0 0.3166e+0	0.4302e-2 -0.2029e-2	0.3859e-3 0.1303e-2			
5	-0.7814e+1 -0.7098e+2	0.9706e+0 -0.3583e+1	0.3705e+0 0.2333e+0	0.2820e-2 -0.1680e-1	0.2581e-3 -0.9201e-3	0.2222e-4 -0.2824e-3		
6	-0.7717e+1 -0.7014e+2	0.9771e+0 -0.3253e+1	0.3678e+0 0.3050e+0	0.1375e-2 -0.3691e-2	-0.7883e-4 0.1083e-2	-0.5156e-4 -0.2999e-4	-0.1484e-4 0.2158e-4	
7	-0.7458e+1 -0.7057e+2	0.1110e+1 -0.3407e+1	0.4063e+0 0.2736e+0	0.1012e-1 -0.8157e-2	0.1535e-2 0.6360e-3	0.2034e-3 -0.5110e-4	0.2051e-4 0.2189e-4	0.4445e-5 0.2338e-6

(a) real part of the S -matrix elements.

(b) imaginary part of the S -matrix elements.

TABLE 3.3.1c

S -matrix elements for the Morse potential after 10 time units with $q_0 = -20.0$ and $p_0 = -6.0$

S_n N	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	-0.3264e+2 -0.9618e+2	0.9026e+1 (a) 0.7214e+1 (b)						
2	-0.3564e+2 -0.1092e+3	-0.1659e+1 0.7638e+1	0.5241e+0 0.1330e+0					
3	-0.3497e+2 -0.1082e+3	-0.1748e+1 0.7880e+1	0.4913e+0 0.1439e+0	-0.2425e-2 -0.2881e-2				
4	-0.3538e+2 -0.1058e+3	-0.1831e+1 0.7814e+1	0.4934e+0 0.1281e+0	-0.4777e-3 -0.3194e-2	0.8515e-4 0.2160e-3			
5	-0.3532e+2 -0.1083e+3	-0.1759e+1 0.7820e+1	0.4986e+0 0.1317e+0	-0.1005e-2 -0.2473e-2	-0.1782e-4 0.1745e-3	0.2360e-5 -0.1259e-4		
6	-0.3532e+2 -0.1082e+3	-0.1787e+1 0.7828e+1	0.4963e+0 0.1310e+0	-0.1082e-2 -0.2841e-2	0.2758e-4 0.1557e-3	0.5389e-5 -0.6998e-5	-0.5852e-6 -0.5080e-6	
7	-0.3532e+2 -0.1082e+3	-0.1766e+1 0.7824e+1	0.4973e+0 0.1307e+0	-0.9217e-3 -0.2727e-2	0.1865e-4 0.1803e-3	0.2071e-5 -0.7615e-5	-0.5216e-6 0.7151e-7	0.5402e-7 -0.2420e-8

(a) real part of the S -matrix elements.

(b) imaginary part of the S -matrix elements.

Comparing the coefficients of a on either side of the equation we obtain the working equations of motion. The equations of motion for the first three S (n =1,2,3) are given by

$$i\dot{S}_0 = -\hbar\omega/4 - \hbar\omega/2\ S_2 - \hbar\omega/4\ S_1^2 + p_0^2/2\mu + R_0 + X_0 \qquad (3.3.16a)$$

$$i\dot{S}_1 = -3\hbar\omega/2\ S_3 + \hbar\omega/2\ S_1 - \hbar\omega\ S_1S_2 + Z + R_0R_1 + X_0X_1 \qquad (3.3.16b)$$

$$i\dot{S}_2 = -3\hbar\omega\ S_4 + \hbar\omega/2\ S_1 - 3\hbar\omega/2\ S_1S_3 - 2\hbar\omega\ S_2^2 + \hbar\omega\ S_2 + S_1$$

$$+ R_0\ [R_1^2\ 2! + R_2\ ] + X_0\ [\ X_1^2/2! + X_2\ ]. \qquad (3.3.16c)$$

3.3b. Numerical Studies.

We have studied the convergence of the S-matrix elements which is shown in the Tables 3.3.1a, 3.3.1b and 3.3.1c for three sets of parameters corresponding to the values of q_0 = -13.45, -5.56 and -20.0. $\hbar$, ω and μ were taken to be equal to 1. p_0 for the first two cases was taken to be zero and for the third case it was taken to be -6.0 [6]. The three values correspond to the position of the wave packet being close to the dissociation limit, half way to the dissociation limit and above the dissociation limit respectively. The convergence behaviour is seen to be good for q = -13.45 and -20.0. But for q = -5.56, the S-matrix elements appear to be oscillating around a mean value. This may be attributed to the fact that when the initial wave packet is at -5.56 it is in the more anharmonic region of the potential

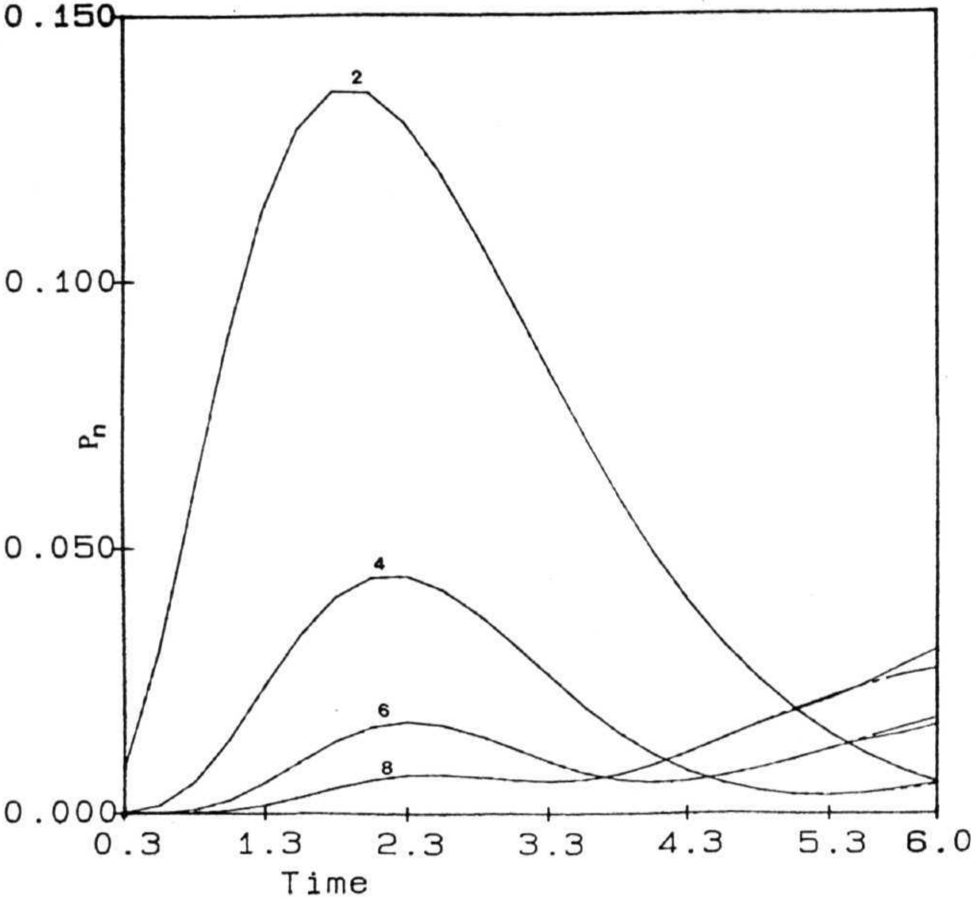


Fig. 3.3.1a: The transition probabilities P for n = 8,6,4 and 2 which are marked above each curve, as a function of time for x_0 = -13.45 and p_0 = 0.0 for the Morse potential. Solid line - basis set expansion and dash and double dot - TDCCM at the truncation index N = 7.

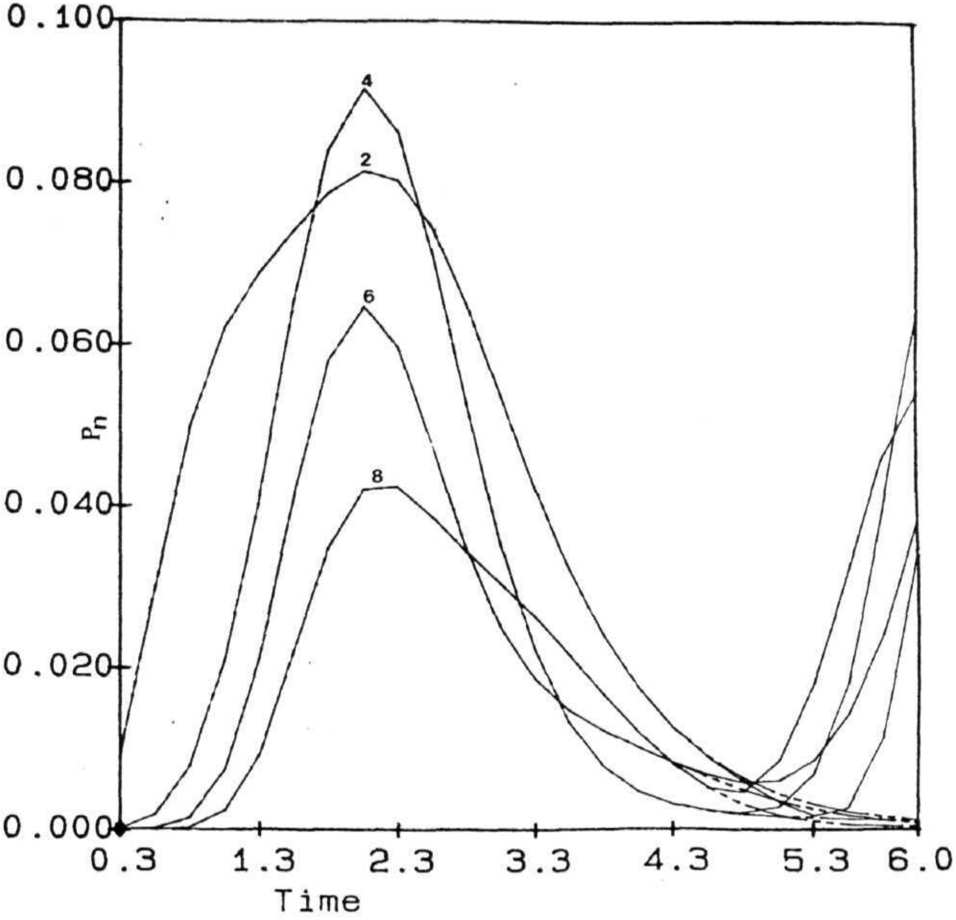


Fig. 3.3.1b: The transition probabilities P_n for n = 8,6,4 and 2 which are narked above each curve, as a function of time for $x_\circ$ -5.56 and p. = 0.0 for the Morse potential. Solid line - basis sat expansion and dash and double dot - TDCCM at the truncation index N = 7 .

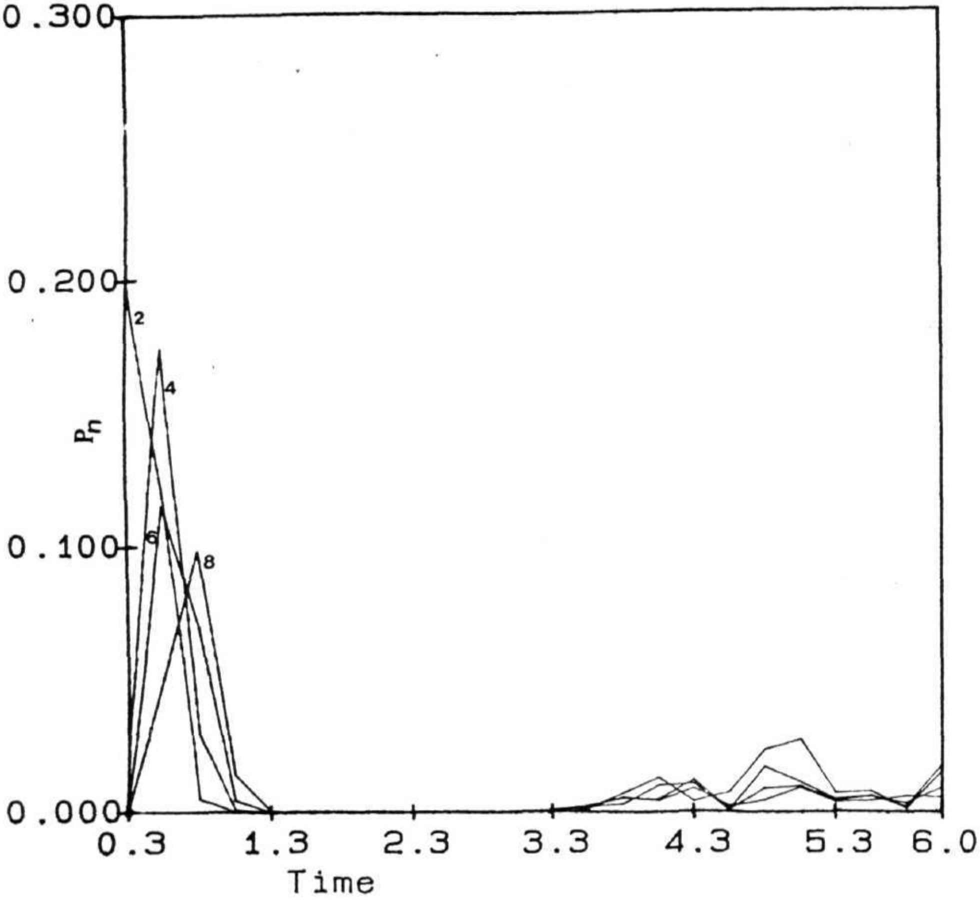


Fig. 3.3.1c: The transition probabilities P for n • 8,6,4 and 2 which are marked above each curve, as a function of time for x_0 - -20.0 and p_0 = -6.0 for the Morse potential. Solid line - basis set expansion and dash and double dot - TDCCM at the truncation index N = 7.

compared to the other two cases. Hence, the wave packet **experiences** greater **anharmonicities** due to which the S-natrix convergence is slightly oscillatory. Like in the case of the single **exponentially** repulsive surface, the higher **S-matrix** elements are very small in magnitude, leading to negligible contribution to the dynamics of the system.

The transition **probabilities** P from the ground to the nth eigenstate of the **hamiltonian** for n = 2,4,6,8 obtained from the algebraic and the basis set expansion methods are shown in Fig 3.3.1a, 3.3.1b and 3.3.1c where P are plotted against time for the three sets of parameters. Both the approaches are comparable. The deviation of the basis set expansion method from the algebraic method is due to insufficient basis.

In Fig.3.3.2a, 3.3.2b and 3.3.2c, we have plotted the modulus of the auto-correlation function obtained from both the methods, against time. Good agreement is seen except that the basis set expansion approach requires even higher basis to approach convergence.

The plot of the modulus of the **autocorrelation** function obtained from the algebraic method at N=7 vs.time is shown in Fig. 3.3.3a, b and c for the three sets of parameters. This is to show that the converged calculations from the algebraic method could be carried out for longer times with only 7 equations of motion.

Similar to the case of the exponentially repulsive surface discussed in Sec. 3.2, the algebraic results show a faster convergence pattern than the basis set expansion method.

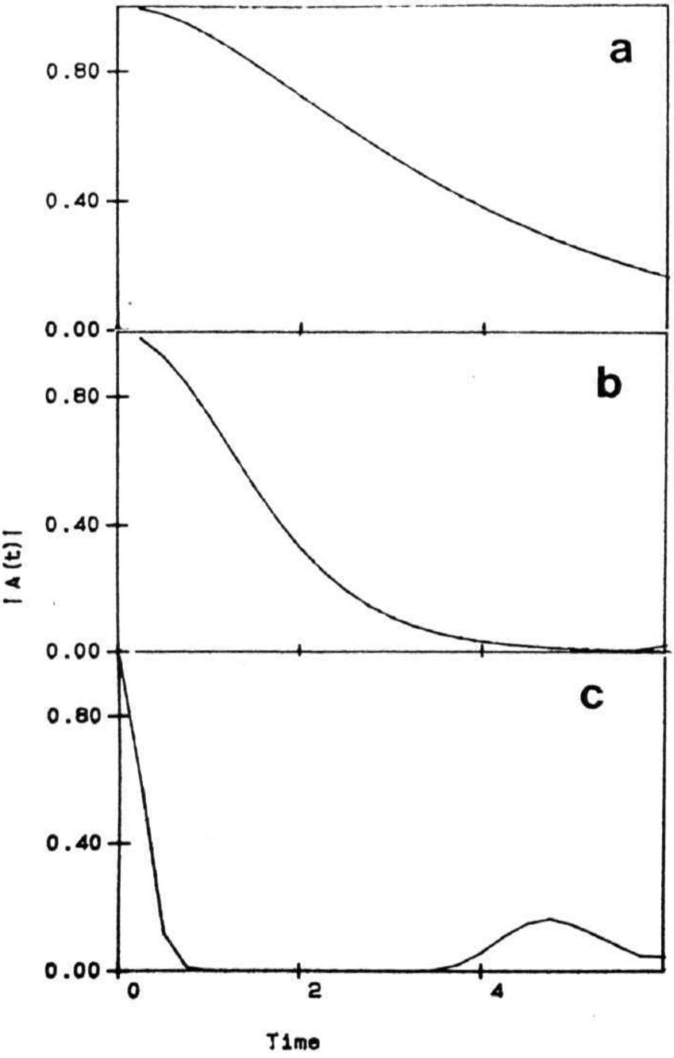


Fig. 3.3.2: Plots of the Modulus of the autocorrelation function vs. tine for the Morse potential for different values of x_0 and p_0. a) x_0 =-13.45 and p_0= 0.0 b) x_0 = -5.56 and P_0 = 0.0 and c) x_0= -20.0 and p_0 = -6.0. Solid line - basis set expansion and dash and double dot •• TDCCM at the truncation index N = 7.

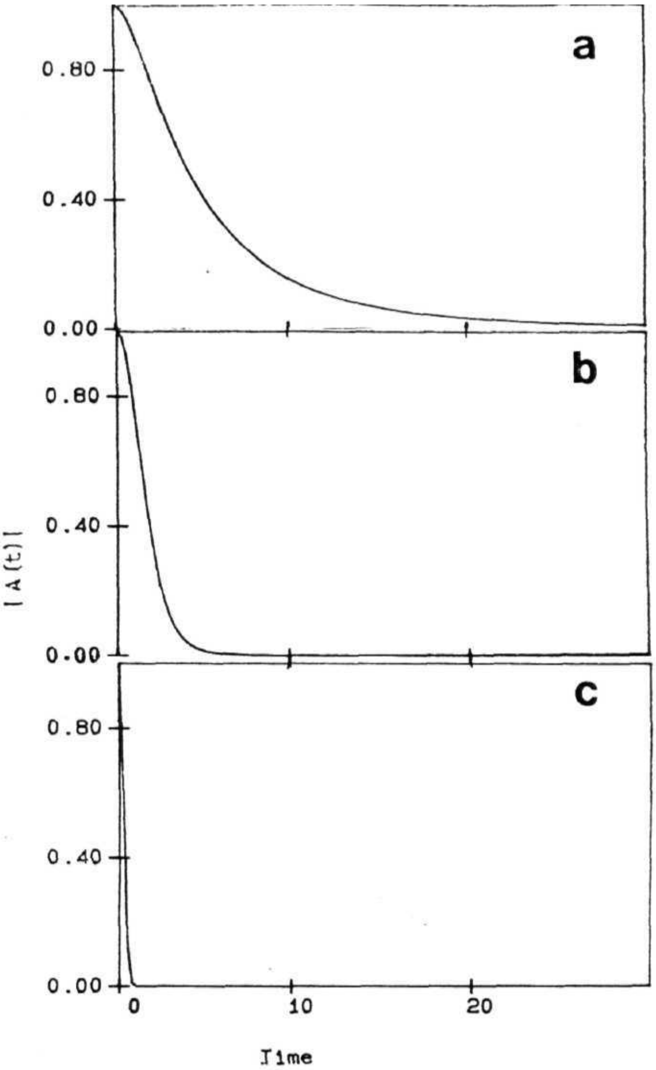


Fig. 3.3.3: Plots of the modulus of the converged autocorrelation function vs. time for the Morse potential at the truncation index N = 7. a) x_0 = -13.45 and p_0 = 0.0, b) x_0 = -5.56 and p_0 = 0.0 and c) x_0 =- 20.0 and p_0 = -6.0.

3.4. DYNAMICS OF ATOM - DIATOM COLLISION IN THE CLASSICAL PATH APPROXIMATION.

In this section we study the dynamics of a collinear collision between an atom A and a diatomic molecule BC. This system has been studied by several authors [7-23]. The collision can be described by the equation

$$A + BC\ (\nu) \longrightarrow A + BC\ (\nu'). \qquad (3.4.1)$$

The diatom is approximated as a harmonic oscillator. The interaction potential between A and BC is described by an exponential potential given by

$$V\ (r_{AB}) = D\ \exp\ (\ -r_{AB}/a) \qquad (3.4.2)$$

where r is the distance between A and B and D and a are constants. Let the distance between A and the centre of mass of BC be R, then R can be written as

$$R = r_{AB} - \gamma\ (r_e - q) \qquad (3.4.3)$$

where q is the deviation of the bond distances of BC from the equilibrium position r and γ is given by

$$\gamma = m_c\ /\ (m_c + m_b). \qquad (3.4.4)$$

The potential now has the form

$$V(R, q) = E \exp(-R(t)/a) \exp(\gamma q/a) \qquad (3.4.5)$$

where, E is the initial collision energy and is a system constant. Treating the translational motion classically, the classical trajectory R(t) is obtained by neglecting BC vibrations during collision and is given by [22,23]

$$\exp(-R(t)/a) = \mathrm{sech}^2 [(E/2\mu)^{1/2} t/a] \qquad (3.4.6)$$

where μ is the collision mass. The hamiltonian of the system is written as,

$$H = \hbar\omega a^{+}a + F(t) \exp[Z(a^{+}+a)] \qquad (3.4.7a)$$

where

$$F(t) = E\ \mathrm{Sech}^2[(E/2m)^{1/2} t/a] \qquad (3.4.7b)$$

and

$$Z = (\gamma/a) \sqrt{(\hbar/(2 M \omega))}. \qquad (3.4.7c)$$

Most of the Lie-algebraic studies to date have been tested on this hamiltonian which have invoked either a linear or a quadratic approximation to the potential [7-12,15-21]. Since microscopic reversibility is lost in the classical path approximation, it is customary to define the total energy of the system E as [7].

$$E = (1/8)\, m\, (v_f+v_i)^2. \qquad (3.4.8)$$

Here v_- and v. are the initial and final velocities appropriate to the transition under consideration, m and M are the reduced mass and the mass of the diatom respectively, and ω is the angular frequency of the diatom. *y* and a characterize the interaction strength. The collision energy for the systems under study was varied in the range 2 ≤ E ≤ 20 ħω. The working equations of motion are obtained in the next subsection.

3.4a. Working Equations.

Since we are interested in the dynamics of the vacuum state, the evolution operator takes the form

$$U_0 = \exp\,[\sum_{n=1}^{N} S_n(a^+)^n + S_0]. \tag{3.4.9}$$

In all the calculations, the truncation index N was varied between 2 and 7. These were integrated from -T to +T ensuring that the appropriate transition probabilities were converged. The propagation of the vacuum state requires solving

$$i\, U_0^{-1}\, \dot{U}_0 = U_0^{-1}\, H\, U_0. \tag{3.4.10}$$

For the exponentially perturbed harmonic oscillator, we get

$$i\sum_m \dot{S}_m a^{+m} = \exp[-\sum_m S_m a^{+m}\,][(a^+a + 1/2)\hbar\omega + F(t)\exp\{Z(a^+ + a)\}]$$

$$\times \qquad \exp[\sum_m S_m a^{+m}]. \tag{3.4.11}$$

Using the BCH [1] formula we obtain the working equations for the cluster amplitudes S_m

$$i \sum_m \dot{S}_m a^{+m} = (a^+ a + 1/2)\hbar\omega + \sum_m m S_m a^{+m} \hbar\omega + Y_0 \exp[Z a^+ + \sum_{n=2} S_n \sum_{m=1} {}^{n}C_m Z^{n-m} a^{+m}] \exp(Za) \tag{3.4.12}$$

where

$$Y_0 = F(t)\exp(Z^2/2)\exp(\sum_{n=1} S_n Z^n) \tag{3.4.13}$$

Comparing the coefficients of a we obtain the following equations for the coefficients S_m .

$$i\dot{S}_0 = 1/2 \hbar\omega + Y_0 \tag{3.4.14a}$$

$$i\dot{S}_1 = S_1 \hbar\omega + Y_0 Y_1 \tag{3.4.14b}$$

$$i\dot{S}_2 = 2S_2 \hbar\omega + Y_0 [Y_1^2/2! + Y_2] \tag{3.4.14c}$$

$$i\dot{S}_3 = 3S_3 \hbar\omega + Y_0 [Y_1^3/3! + Y_1 Y_2 + Y_3] \tag{3.4.14d}$$

$$i\dot{S}_4 = 4S_4 \hbar\omega + Y_0 [Y_1^4/4! + Y_1 Y_3 + Y_2^2/2! + Y_4 + Y_1^2 Y_2/2!] \tag{3.4.14e}$$

$$i\dot{S}_5 = 5S_5 \hbar\omega + Y_0 [Y_1^5/5! + Y_1^3 Y_2/3! + Y_1^2 Y_3/2! + Y_1 Y_4 + Y_2 Y_3 + Y_5 + Y_2^2 Y_1/2!]. \tag{3.4.14f}$$

TABLE - 3.4.1a

S-MATRIX ELEMENTS AT THE END OF THE TIME DEVELOPMENT FOR DIFFERENT VALUES OF TRUNCATION INDEX N.

	S_n					
N	2	3	4	5	6	7
n						
E = 7ħw						
0	-0.7183 a -0.4109E+2 b	-0.7215 -0.4108E+2	-0.7214 -0.4108E+2	-0.7214 -0.4108E+2	-0.7214 -0.4108E+2	-0.7214 -0.4108E+2
1	-0.6680E-1 -0.1180E+1	-0.7356E-1 -0.1190E+1	-0.7342E-1 -0.1190E+1	-0.7342E-1 -0.1190E+1	-0.7342E-1 -0.1190E+1	-0.7342E-1 -0.1190E+1
2	-0.9601E-2 -0.6982E-2	-0.8224E-2 -0.7845E-2	-0.8177E-2 -0.7836E-2	-0.8183E-2 -0.7832E-2	-0.8183E-2 -0.7832E-2	-0.8183E-2 -0.7832E-2
3		0.1671E-4 0.7837E-4	-0.1273E-1 0.1073E-3	-0.1525E-4 0.1046E-3	-0.1501E-2 0.1044E-3	-0.1499E-2 0.1044E-3
4			0.4216E-6 -0.1162E-5	0.1421E-5 -0.1722E-5	0.1499E-5 -0.1593E-5	0.1484E-5 -0.1587E-5
5				-0.2177E-7 0.2703E-8	-0.5331E-7 0.8326E-8	-0.5479E-7 0.2900E-8
6					0.2800E-9 0.6366E-9	0.1124E-8 0.7951E-9
7						0.1183E-10 -0.2445E-10

TABLE **3.4.1a contd.**

E = 20 ħw

0	-0.4346E+1 -0.4847E+2	-0.4389E+1 -0.4832E+2	-0.4393E+1 -0.4832E+2	-0.4393E+1 -0.4832E+2	-0.4393E+1 -0.4832E+2	-0.4393E+1 -0.4832E+2
1	-0.4089 -0.2747E+1	-0.4964 -0.2808E+1	-0.4931 -0.2814E+1	-0.4919 -0.2813E+1	-0.4921 -0.2813E+1	-0.4921 -0.2813E+1
2	-0.5806E-1 -0.4255E-1	-0.4670E-1 -0.5553E-1	-0.4337E-1 -0.5396E-1	-0.4392E-1 -0.5331E-1	-0.4404E-1 -0.5344E-1	-0.4400E-1 -0.5346E-1
3		-0.4350E-4 0.81216E-3	-0.4858E-3 0.1333E-2	-0.6531E-3 0.1158E-2	-0.5946E-3 0.1116E-2	-0.5869E-3 0.1134E-2
4			0.1571E-4 -0.1145E-4	0.4254E-4 -0.2511E-4	0.4898E-4 -0.1210E-4	0.4374E-4 -0.1041E-4
5				-0.6453E-6 -0.7009E-6	-0.1754E-5 -0.5473E-6	-0.1864E-5 -0.1332E-5
6					-0.6756E-8 0.6637E-7	0.2397E-7 0.7282E-7
7						0.2539E-8 -0.2812E-8

---

a) Real part of S.
b) Imaginary part of S.

TABLE 3.4.1b

S-MATRIX ELEMENTS AT THE END OF THE TIME DEVELOPMENT FOR DIFFERENT VALUES OF TRUNCATION INDEX N FOR C + D_2 COLLISION.

	S_n					
N	2	3	4	5	6	7
n						
E = 7ℏω						
0	-0.2997 -0.2287e+2	-0.2999 -0.2287e+2	-0.2999 -0.2287e+2	-0.2999 -0.2287e+2	-0.2999 -0.2287e+2	-0.2999 -0.2287e+2
1	-0.7151 0.2936	-0.7157 0.2835	-0.7157 0.2935	-0.7157 0.2935	-0.7157 0.2935	-0.7157 0.2935
2	0.7644e-2 0.6518e-2	0.7467e-2 0.6213e-2	0.7474e-2 0.6219e-2	0.7474e-2 0.6219e-2	0.7474e-2 0.6219e-2	0.7474e-2 0.6219e-2
3		-0.1260e-4 -0.5791e-4	-0.1159e-4 -0.5491e-4	-0.1162e-4 -0.5497e-4	-0.1162e-4 -0.5497e-4	-0.1162e-4 -0.5497e-4
4			0.9687e-7 0.3614e-6	0.8089e-7 0.3461e-6	0.8162e-7 0.3464e-6	0.8159e-7 0.3464e-6
5				-0.8612e-9 -0.3070e-8	-0.6528e-9 -0.2911e-8	-0.6631e-9 -0.2914e-8
6					0.1059e-10 0.2838e-10	0.8071e-11 0.2710e-10
7						-0.1228e-12 -0.2849e-12

Table 3.4.1b contd.

E = $20\hbar\omega$

0	-0.1616e+1 -0.3298e+2	-0.1619e+1 -0.3298e+2	-0.1619e+1 -0.3298e+2	-0.1619e+1 -0.3298e+2	-0.1619e+1 -0.3298e+2	-0.1619e+1 -0.3298e+2
1	-0.1598e+1 0.7947	-0.1604e+1 0.7912	-0.1604e+1 0.7913	-0.1604e+1 0.7913	-0.1604e+1 0.7913	-0.1604e+1 0.7913
2	0.3921e-1 0.2710e-1	0.3625e-1 0.2446e-1	0.3635e-1 0.2459e-1	0.3635e-1 0.2459e-1	0.3635e-1 0.2459e-1	0.3635e-1 0.2459e-1
3		-0.1864e-3 -0.5388e-3	-0.1574e-3 -0.4931e-3	-0.1595e-3 -0.4951e-3	-0.1595e-3 -0.4951e-3	-0.1595e-3 -0.4951e-3
4			0.3254e-5 0.6269e-5	0.2478e-5 0.5719e-5	0.2554e-5 0.5749e-5	0.2549e-5 0.5748e-5
5				-0.7018e-7 -0.1049e-6	-0.5099e-7 -0.9594e-7	-0.5309e-7 -0.9629e-7
6					0.1704e-8 0.1738e-8	0.1236e-8 0.1639e-8
7						-0.4125e-10 -0.3064e-10

a) Real part of S.
b) Imaginary part of S.

$$i\dot{S}_6 = 6S_6\,\hbar\omega + Y_0\,[\,Y_1^6/6! + Y_1^4Y_2/4! + Y_1^3Y_3/3! + Y_1^2Y_4/2!$$

$$+ Y_1Y_5 + Y_2^3/3! + Y_2^2Y_1^2/2!2! + Y_2Y_4 + Y_3^2/2! + Y_6 + Y_1Y_2Y_3\,] \quad (3.8g)$$

$$(3.4.14g)$$

$$i\dot{S}_7 = 7S_7\,\hbar\omega + Y_0\,[\,Y_1^7/7! + Y_1^5Y_2/5! + Y_1^4Y_3/4! + Y_1^3Y_4/3! + Y_1^2Y_5/2!$$

$$+ Y_1Y_6 + Y_2^3Y_1/3! + Y_2^2Y_3/2! + Y_2Y_5 + Y_3^2Y_1/2! + Y_3Y_4$$

$$+Y_5Y_2 + Y_4Y_1Y_2 + Y_1^2Y_2Y_3/2! + Y_1^3Y_2^2/3!2!\,] \qquad (3.4.14h)$$

Here, the Y are as defined in eq. (3.2.20) except that instead of the time independent constant F we now have a time dependent function F(t) and the expressions for the constant Z differ. they are given by equations (3.4.7b) and (3.4.7c) for the two cases respectively.

The transition probabilities P_ _ are given by

$$P_{0\text{-->}n} = |\langle n|\,U_0\,|0\rangle|^2 \qquad (3.4.15)$$

where the evaluation for the first three probabilities is shown in section 3.2a which correspond to the coefficients P .

3.4b. Numerical Studies.

As an initial step we studied the sensitivity of S-matrix elements on the truncation index N in eq(3.4.12) for the collision between He + H_2 and C + D_2. The results of the two systems are

TABLE - 3.4.2a

TRANSITION PROBABILITIES 0 --> 0, 1, 2, 3 AS A FUNCTION OF THE TRUNCATION INDEX N.

N ENERGY	2	3	4	5	6	7
4	0.7544 a 0.1404 b 0.2764E-2 c	0.7538 0.1415 0.2791E-2 0.8219E-6 d	0.7538 0.1415 0.2791E-2 0.8221E-6	0.7538 0.1415 0.2791E-2 0.8221E-6	0.7538 0.1415 0.2791E-2 0.8221E-6	0.7538 0.1415 0.2791E-2 0.8221E-6
10	0.4742E-1 0.1666 0.2431	0.4659E-1 0.1680 0.2495 0.1941	0.4659E-1 0.1680 0.2493 0.1939	0.4659E-1 0.1680 0.2493 0.1939	0.4659E-1 0.1680 0.2493 0.1939	0.4659E-1 0.1680 0.2493 0.1939
16	0.1496E-2 0.1132E-1 0.4038E-1	0.1418E-2 0.1120E-1 0.4126E-1 0.9377E-1	0.1414E-2 0.1119E-1 0.4125E-1 0.9370E-1	0.1415E-2 0.1119E-1 0.4125E-1 0.9370E-1	0.1415E-2 0.1119E-1 0.4125E-1 0.9370E-1	0.1415E-2 0.1119E-1 0.4125E-1 0.9370E-1
20	0.1676E-3 0.1644E-2 0.7816E-2	0.1538E-3 0.1594E-2 0.7910E-2 0.2499E-1	0.1525E-3 0.1588E-2 0.7898E-2 0.2497E-1	0.1527E-3 0.1588E-2 0.7897E-2 0.2497E-1	0.1527E-3 0.1588E-2 0.7897E-2 0.2497E-1	0.1527E-3 0.1588E-2 0.7897E-2 0.2497E-1

a, b, c and d represent 0-->0, 0-->1, 0-->2 and 0-->3 transition probabilities respectively.

TABLE 3.4.2b

TRANSITION PROBABILITIES 0 -->0, 1, 2, 3 AS A FUNCTION OF THE TRUNCATION INDEX N FOR D_2 + C COLLISION.

N Energy (ħω units)	2	3	4	5	6	7
4.0	0.8549 [a] 0.9295e-1 [b] 0.1466e-2 [c]	0.8549 0.9299e-1 0.1466e-2 0.7896e-6 [d]	0.8549 0.9299e-1 0.1466e-2 0.7897e-6	0.8549 0.9299e-1 0.1466e-2 0.7897e-6	0.8549 0.9299e-1 0.1466e-2 0.7897e-6	0.8549 0.9299e-1 0.1466e-2 0.7897e-6
10.0	0.3137 0.3652 0.1759	0.3133 0.3656 0.1763 0.4533e-1	0.3133 0.3656 0.1763 0.4533e-1	0.3133 0.3656 0.1763 0.4533e-1	0.3133 0.3656 0.1763 0.4533e-1	0.3133 0.3656 0.1763 0.4533e-1
16.0	0.9135e-1 0.2301 0.2643	0.9129e-1 0.2301 0.2653 0.1856	0.9129e-1 0.2301 0.2653 0.1856	0.9129e-1 0.2301 0.2652 0.1856	0.9129e-1 0.2301 0.2652 0.1856	0.9129e-1 0.2301 0.2652 0.1856
20.0	0.3943e-1 0.1351 0.2172	0.3918e-1 0.1349 0.2172 0.2184	0.3918e-1 0.1349 0.2172 0.2184	0.3918e-1 0.1349 0.2172 0.2184	0.3918e-1 0.1349 0.2172 0.2184	0.3918e-1 0.1349 0.2172 0.2184

a, b, c and d represent 0-->0, 0-->1, 0-->2 and 0-->3 transition probabilities respectively.

presented in Tables 3.4.1a and 3.4.1b (for E = $7\hbar\omega$ and $20\hbar\omega$) respectively From the tables, it is apparent that the cluster amplitudes are fairly insensitive to the truncation index after about N > 4.

The transition probabilities from 0->0,1,2,3 for some representative energies as a function of N are presented in tables 3.4.2a, and 3.4.2b for He + H_2 and C + D_2 systems respectrively. As can be seen, these are also insensitive to the truncation index for N > 4. It is seen that for higher energies S is inadequate, indicating the importance of higher S-matrix elements.

Lastly, in Tables 3.4.3a and 3.4.3b, we present 0->n transition probabilities for several energies with N=7 for both the systems. We have also calculated the transition probabilities by expanding the wave function as a linear superposition of harmonic oscillator basis functions which are also shown in the same Tables. Good agreement of the algebraic method is seen with the basis set expansion approach.

3.5. CONCLUSIONS.

All the three systems studied in this chapter differ in the final state interactions. The final state interactions in the hamiltonian described by the exponentially repulsive potential are purely kinetic. The Morse potential has anharmonic final state interactions. In contrast, the system described by the time driven harmonic oscillator has purely harmonic final state interactions. In spite of having different final state interactions the

TABLE - 3.4.3a

TRANSITION PROBABILITIES FOR H_2(m) + He --> H_2(n) + He

m-->n ENERGY (ħw units)	0-->0	0-->1	0-->2	0-->3	0-->4	0-->5	0-->6	0-->7	0-->8	0-->9	0-->10
2.0	0.9896[a] 0.9896[b]	0.7875E-3 0.7875E-3									
4.0	0.7538 0.7538	0.1415 0.1415	0.2791E-2 0.2791E-2	0.8221E-6 0.8221E-6							
6.0	0.3752 0.3752	0.3534 0.3534	0.9179E-1 0.9179E-1	0.6502E-2 0.6535E-2	0.7354E-4 0.7354E-4	0.1512E-7 0.1512E-7					
8.0	0.1416 0.1416	0.3064 0.3064	0.2417 0.2417	0.8371E-1 0.8371E-1	0.1215E-1 0.1215E-1	0.5866E-3 0.5866E-3	0.5125E-5 0.5125E-5	0.9000E-9 0.9000E-9			
10.0	0.4659E-1 0.4659E-1	0.1680 0.1680	0.2493 0.2493	0.1939 0.1939	0.8327E-1 0.8327E-1	0.1905E-1 0.1905E-1	0.2056E-2 0.2056E-2	0.8045E-4 0.8045E-4	0.6124E-6 0.6124E-6	0.1125E-9 0.1014E-9	
12.0	0.1453E-1 0.1453E-1	0.7404E-1 0.7404E-1	0.1654 0.1654	0.2110 0.2110	0.1673 0.1675	0.8416E-1 0.8412E-1	0.2618E-1 0.2618E-1	0.4699E-2 0.4699E-2	0.4233E-3 0.4233E-3	0.1492E-4 0.1456E-4	0.1035E-6 0.1029E-6
14.0	0.4499E-2 0.4499E-2	0.2942E-1 0.2942E-1	0.8760E-1 0.8760E-1	0.1561 0.1561	0.1842 0.1842	0.1498 0.1498	0.8472E-1 0.8472E-1	0.3276E-1 0.3276E-1	0.8297E-2 0.8297E-2	0.1282E-2 0.1269E-2	0.1023E-3 0.1013E-3
16.0	0.1414E-2 0.1414E-2	0.1119E-1 0.1119E-1	0.4125E-1 0.4125E-1	0.9370E-1 0.9370E-1	0.1460 0.1460	0.1644 0.1644	0.1368 0.1368	0.8453E-1 0.8453E-1	0.3833E-1 0.3833E-1	0.1247E-1 0.1240E-1	0.2757E-2 0.2722E-2
18.0	0.4572E-3 0.4572E-3	0.4205E-2 0.4205E-2	0.1829E-1 0.1829E-1	0.4999E-1 0.4999E-1	0.9588E-1 0.9588E-1	0.1366 0.1366	0.1491 0.1491	0.1265 0.1265	0.8363E-1 0.8363E-1	0.4286E-1 0.4275E-1	0.1684E-1 0.1658E-1
20.0	0.1527E-3 0.1527E-3	0.1588E-2 0.1588E-2	0.7897E-2 0.7897E-2	0.2497E-1 0.2497E-1	0.5627E-1 0.5627E-1	0.9596E-1 0.9596E-1	0.1281 0.1281	0.1368 0.1368	0.1179 0.1179	0.8291E-1 0.8216E-1	0.4691E-1 0.4607E-1

a) Results of Lie-algebraic calculations with operators upto S_7 included.
b) Results of converged basis set calculations.

TABLE 3.4.3b

TRANSITION PROBABILITIES FOR $D_2(m) + C \rightarrow D_2(n) + C$.

m-->n Energy (ħω units)	0 -->0	0 -->1	0 -->2	0 -->3	0 -->4	0 -->5	0 -->6	0 -->7	0 -->8	0 -->9	0 -->10
2.0	0.9886e+0 0.9886e+0	0.1547e-2 a 0.1547e-2 b									
4.0	0.8549e+0 0.8549e+0	0.9298e-1 0.9298e-1	0.1466e-2 0.1466e-2	0.7897e-6 0.7897e-6							
6.0	0.6485e+0 0.6485e+0	0.2480e+0 0.2480e+0	0.2895e-1 0.2895e-1	0.1095e-2 0.1095e-2	0.9108e-5 0.9118e-5	0.3081e-8 0.3107e-8					
8.0	0.4590e+0 0.4590e+0	0.3445e+0 0.3445e+0	0.9744e-1 0.9744e-1	0.1284e-1 0.1284e-1	0.7828e-3 0.7828e-3	0.1876e-4 0.1876e-4	0.2947e-5 0.1112e-6	0.2912e-10 0.2922e-10			
10.0	0.3133e+0 0.3133e+0	0.3656e+0 0.3656e+0	0.1763e+0 0.1763e+0	0.4583e-1 0.4583e-1	0.6649e-2 0.6649e-2	0.5505e-3 0.5505e-3	0.2528e-4 0.2364e-4	0.4312e-6 0.4312e-6	0.2059e-8 0.2059e-8	0.2172e-11 0.4572e-12	
13.0	0.1708e+0 0.1708e+0	0.3131e+0 0.3131e+0	0.2538e+0 0.2538e+0	0.1197e+0 0.1197e+0	0.3635e-1 0.3635e-1	0.7397e-2 0.7397e-2	0.1083e-2 0.1015e-2	0.9189e-4 0.9189e-4	0.5186e-5 0.5186e-5	0.2550e-6 0.1633e-6	0.2677e-8 0.2312e-8
14.0	0.1388e+0 0.1388e+0	0.2860e+0 0.2860e+0	0.2642e+0 0.2642e+0	0.1445e+0 0.1445e+0	0.5197e-1 0.5197e-1	0.1288e-1 0.1288e-1	0.2384e-2 0.2237e-2	0.2703e-3 0.2703e-3	0.2205e-4 0.2205e-4	0.1619e-5 0.1141e-5	0.3680e-7 0.3347e-7
16.0	0.9129e-1 0.9129e-1	0.2301e+0 0.2301e+0	0.2652e+0 0.2652e+0	0.1856e+0 0.1856e+0	0.8799e-1 0.8799e-1	0.2987e-1 0.2987e-1	0.7942e-2 0.7466e-2	0.1387e-2 0.1387e-2	0.1906e-3 0.1906e-3	0.2403e-4 0.1894e-4	0.1509e-5 0.1319e-5
18.0	0.5985e-1 0.5985e-1	0.1784e+0 0.1784e+0	0.2469e+0 0.2469e+0	0.2109e+0 0.2109e+0	0.1245e+0 0.1245e+0	0.5394e-1 0.5394e-1	0.1881e-1 0.1772e-1	0.4496e-2 0.4496e-2	0.8865e-3 0.8865e-3	0.1605e-3 0.1354e-3	0.1790e-4 0.1579e-4
20.0	0.3918e-1 0.3918e-1	0.1349e+0 0.1349e+0	0.2178e+0 0.2178e+0	0.2197e+0 0.2197e+0	0.1554e+0 0.1554e+0	0.8201e-1 0.8201e-1	0.3546e-1 0.3347e-1	0.1081e-1 0.1081e-1	0.2794e-2 0.2794e-2	0.6814e-3 0.5810e-3	0.1090e-3 0.9896e-4

a) Results of Lie-algebraic calculations with operators upto S_7 included.

b) Results of converged basis set calculations.

algebraic method shows a good convergence pattern of the S-matrix elements for all the three systems.

In all the systems, the algebraic results converge to the exact value by about S. while the calculations based on basis set expansion required functions between 40 to 120 for convergence. These results indicate that the Lie-algebraic approach has a far better convergence pattern than a linear basis set expansion. A few comments on the computational resources required for the Lie-algebraic approach are in order. In general, we found that the working equations by the Lie-algebraic method were no stiffer than the corresponding basis set expansion approach. Thus, step lengths of the same magnitude were required in both cases. Though the Lie-algebraic approach requires the integration of nonlinear equations, these require much less time than the basis set expansion since the number of variables required to achieve convergence is much less in this case. Also the converged algebraic calculations could be carried out for longer times with very few variables contrary to the basis set expansion method.

We now comment on the accuracy of the algebraic approach. The correlation functions were found to be very close to the exact which we have shown in sections 3.2 and 3.3. The P_n coefficients obtained from the linear basis set expansion approach and the corresponding coefficients obtained from the algebraic approoh were also in close agreement. These results have been presented in sections 3.2 and 3.3. The transition probabilities calculated in the atom-diatom collisions from the algebraic method for all numerical purposes were found to be exact.

REFERENCES

1. R.M.Wilcox ,J. Math. Phys.,8, 962(1967).
2. D. Huber and E.J. Heller, J. Chem. Phys.,89, 2003 (1988).
3. D. Huber, Song Ling, Dan G. Imre and E. J. Heller, J. Chem. Phys. 90, 7317 (1989).
4. A. Warshel and J.K. Hwang, J. Chem. Phys., 82, 1756 (1985)
5. J. K. Hwang and A. Warshel, Chem. Phys. Lett., 115, 281 (1985).
6. J. Kucar and H. D. Meyer, J. Chem. Phys., SO, 5566 (1989).
7. B. Gazdy and D.A. Micha, J. Chem. Phys., 82, 4926 (1985).
8. F Vilallonga and D.A. Micha, Int. J. Quantum Chem. Symp, 15, 653 (1981).
9. E. Vilallonga and D. A. Micha, J.Chem. Phys.,79, 3794(1983).
10. J. A. Recamier, D.A. Micha and B. Gazdy, J. Chem. Phys., 85, 5093 (1986).
11. J. Echave, F.M. Fernandez and D. A. Micha, J. Chem. Phys. 94, 3537 (1991).
12. P.Pechukas and J.C.Light, J. Chem. Phys.,44, 3897(1966).
13. A. P. Clark and A. S. Dickinson, J. Phys. B6, 164 (1973).
14. D.Secrest and B.R. Johnson, J.Chem. Phys., 45, 4556(1966).
15. D.A. Micha Int. J. Quantum Chem.,23, 551(1983).
16. J.A. Recamier, D.A. Micha and B. Gazdy. Chem. Phys. Lett., 119, 383 (1985).
17. H.K. Shin, Chem. Phys. Lett., 3, 125(1969).
18. I. Benjamin, J. Chem. Phys., 85, 5611(1986).
19. J.Yuan and R. Gilmore, J. Chem. Phys., 88, 130(1987).

20. S. Shi and H.A. Rabitz, J. Chem. Phys., **92**, 364(1990).

21. J. Echave, F.M. Fernandez and D. A. Micha, J. Chem. Phys., *94.,* 3537 (1991).

22. D.Rapp, J. Chem. Phys., **32,** 735(1959).

23. D. Rapp and T.E. Sharp J. Chem. Phys. **38** ,2641 (1963)

CHAPTER 4.

APPLICATION TO MODEL TWO-DIMENSIONAL SYSTEMS

4.1. INTRODUCTION

In this chapter, we study the applicability of the time dependent coupled cluster method to two-dimensional potentials modelling realistic systems and obtain the absorption spectra. We have applied the formalism to the photodissociation dynamics of linear triatomics in the Beswick and Jortner model [1] and to the two dimensional Henon-Heils potential energy surface [2].

The standard approach for the calculation of absorption spectrum is via basis set expansion. In this approach, the Franck-Condon spectrum of the electronic state e is given by

$$P(\omega) = \mu_{eg}^2 \sum_n |\langle \chi_n | \chi_g \rangle|^2 \, \delta(\omega_n - \omega_g - \omega). \qquad (4.1.1)$$

Here, χ is the vibrational ground state of the lower electronic surface and x are the vibrational wave functions associated with the upper surface. ω and ω are the respective vibrational frequencies. The Condon approximation that the dipole matrix element is weakly dependent on the nuclear coordinates and hence can be approximated as a constant is invoked. Knowledge of x and ω is required to obtain the spectrum. These are obtained by diagonalising the vibrational hamiltonian of the upper surface H in an appropriate Hilbert space [3]. The computational resources required for such a calculation scales exponentially with the number of degrees of freedom in the system. This provides the motivation for the development of alternate methods. One way of obtaining a spectrum is the time dependent formulation of eq.(4.1.1) in which the absorption spectrum is given by the fourier transform of the autocorrelation function A(t) of χ

propagated on the upper electronic surface [4].

The expression for the absorption spectrum is obtained by making the substitution

$$\delta(\omega_n - \omega) = 1/(2\pi) \int e^{-i(\omega_n - \omega)t} \, dt . \qquad (4.1.2)$$

Substituting the above equation in the eq. (4.1.1) for $P(\omega)$ we obtain

$$P(\omega) = \mu_{eg}^2 \int_{-\infty}^{\infty} e^{-i(\omega_n - \omega)t} \, \Sigma \langle \chi_g | \chi_n \rangle \langle \chi_n | \chi_g \rangle dt$$

$$= \mu_{eg}^2 \int_{-\infty}^{\infty} e^{i\omega t} \langle \chi_g | e^{-i H_e t} \sum_n | \chi_n \rangle \langle \chi_n | \chi_g \rangle dt. \qquad (4.1.3)$$

Invoking the completeness theorem according to which

$$\sum_n | \chi_n \rangle \langle \chi_n | = 1 \; . \qquad (4.1.4)$$

we obtain

$$P(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \langle \chi_g | e^{-i H_e t} | \chi_g \rangle dt. \qquad (4.1.5)$$

The term $\langle \chi_g | e^{-iH_e t} | \chi \rangle$ in the above equation is the probability amplitude that the vibrational wave function χ_g remains in the ground state and is called the auto-correlation function A(t). Hence,

$$A(t) = \langle \chi_g | e^{-i H_e t} | \chi_g \rangle . \quad (4.1.6)$$

The equation for the absorption spectrum is now rewritten as

$$P(\omega) = \mu_{eg}^2 \int A(t) \exp(i\omega t)\, dt. \quad (4.1.7)$$

The propagation of χ on the upper electronic surface is carried out by solving the time dependent Schroedinger equation. Because of the large density of states, it is often not possible to resolve the individual vibrational levels in the spectra of dissociative surfaces and only the homogenously broadened envelope of the spectrum is observed. The time dependent approach is particularly suited for the calculations of such spectra since one needs only short time dynamics for evaluating such envelopes.

In Sec. 4.2 we apply the TDCCM to the photodissociation dynamics of a few dissociative surfaces in the Beswick and Jortner model [1]. TDCCM converges faster than a linear superposition of basis functions since the evolution operator is taken to be an exponential ansatz. To test the validity of this, we calculate the autocorrelation functions and spectra and compare with the basis set expansion approach. The methodology is presented in Sec.4.2a and the results along with our conclusions are presented in Sec. 4.2b. In Sec.4.3a we discuss the application of the TDCCM to the Henon-Heils potential and study the norm conservation in Sec. 4.3b. In Sec.4.4 we present a few concluding remarks.

4.2. Application to photodissociation dynamics in the Beswick and Jortner model.

Study of photodissociation dynamics has been one of the main attractions for chemists for long [5]. As considerable experimental data is available, theoretical chemists find photodissociation dynamics, a valuable tool for the development of theory. For example, using the available experimental absorption spectra," we can deduce the approximate potential energy surfaces. The absorption spectra which arise due to the excitation from the ground to a repulsive state are of prime importance in understanding the photofragmentation dynamics of the polyatomic molecules.

4.2a. The Model Hamiltonian.

The Beswick and Jortner model [1J describing the photodissociation of a triatomic molecule ABC into A and BC in collinear geometry assumes that the potential surface from which excitation takes place is a harmonic surface. The ground state hamiltonian of the system is given by

$$H_g = -\hbar^2/2\mu_{A,BC} - \hbar^2/2\mu_{BC} + V_g \tag{4.2.1}$$

where $\mu_{A,BC}$ and μ_{BC} are the reduced masses.

$$\mu_{A,BC} = m_A(m_B + m_C)/(m_A + m_B + m_C) \tag{4.2.2}$$

$$\mu_{BC} = m_B\, m_C\, /(m_B + m_C\,). \qquad (4.2.3)$$

The ground state potential is given by

$$V_g = 1/2\; k_{BC}^{(s)}\; (R_{BC} - \bar{R}_{BC}^{(S)}\;)^2 + 1/2\; k_{AB}^{(s)}\; (\; R_{AB} - \bar{R}_{AB}^{(s)}\;)^2 \qquad (4.2.4)$$

where R_{AB} and R correspond to AB and BC stretch **respectively.** $R_{AB}^{`\sim}$ and $\bar{R}_{BC}^{(s}$ are the bond lengths of AB and BC **respectively.** $k_{BC}^{`\sim}$ and $k_{AB}^{`\sim}$ are the force constants corresponding to the BC and AB bonds in the ground state respectively and are evaluated from the experimental normal mode frequencies ω and ω_2 from the relations

$$(k_{AB}^{(s)}/\mu_{AB}\;) + (k_{BC}^{(s)}/\mu_{BC}) = \omega_1^2 + \omega_2^2 \qquad (4.2.5a)$$

$$k_{AB}^{(s)}\; k_{BC}^{(s)} = [\; m_A m_B m_C\; /\; (m_A + m_B + m_C)\,]\; \omega_1^2\; \omega_2^2\, . \qquad (4.2.5b)$$

Converting the ground state **hamiltonian** in terms of normal coordinates

$$H_g = \hbar\, \omega_1\; [-1/2\; \partial^2/\partial q_1^2 + q_1^2\;] + \hbar\, \omega_2\; [-1/2\; \partial^2/\partial q_2^2 + q_2^2\;]$$

where q and q_2 are the normal coordinates of the bound system and g denotes the ground state. The excited state **hamiltonian** is taken to be [1]

$$H_e = -\hbar^2/2\mu_{A.BC}\; \partial^2/\partial R^2 - \hbar^2/2\mu_{BC}\; \partial^2/\partial R_{BC}^2 + 1/2\; \mu_{BC}\; {\omega_{BC}^{(d)}}^2\, (R_{BC} - R_{BC}^{(d)})^2$$
$$+ A\; \exp\; (-a\; R)\; \exp\; (a m_C/(m_B + m_C))\; R_{BC} \qquad (4.2.6b)$$

where

$$R = R_{AB} + [m_C / (m_B + m_C)] R_{BC} . \tag{4.2.7}$$

A is the pre-exponential factor and a gives the AB poential range. We now rewrite the hamiltonian of the dissociative surface in terns of the ground state normal coordinates. The advantage of using this coordinate representation is that the equation for the autocorrelation function turns out to be particularly simple. Converting the excited state hamiltonian in terms of the harmonic oscillator ladder operators a and a given by

$$a_i = (q_i + \partial/\partial q_i) / \sqrt{2}, \tag{4.2.8a}$$
$$a_i^{+} = (q_i - \partial/\partial q_i) / \sqrt{2}, \tag{4.2.8b}$$

we obtain the following hamiltonian equation for the dissociati

surface.

$$\begin{aligned} H_e = \; & Z_0 + Z_1 a_1^{+} a_1 + Z_2 a_2^{+} a_2 + Z_3 (a_1^{+2} + a_1^{2}) + Z_4 (a_2^{+2} + a_2^{2}) \\ & + Z_5 (a_1^{+} a_2^{+} + a_1^{+} a_2 + a_2^{+} a_1 + a_1 a_2) + Z_6 (a_1^{+} + a_1) \\ & + Z_7 (a_2^{+} + a_2) + Z \exp [Z_8 (a_1^{+} + a_1) + Z_9 (a_2^{+} + a_2)] \end{aligned} \tag{4.2.9}$$

where, Z. and Z are the coefficients of the operators which arise when converting the excited state hamiltonian in terms of the ladder operators. These coefficients are given by the equations

$$Z_3 = -\hbar\omega_1/4 + [k(c_{21}/(c_{12}c_{21} - c_{11}c_{22})^2)]/4 \quad (4.2.10a)$$

$$Z_4 = -\hbar\omega_2/4 + [k(c_{11}/(c_{12}c_{21} - c_{11}c_{22})^2)]/4 \quad (4.2.10b)$$

$$Z_1 = \hbar\omega_1 + 2\,Z_3 \quad (4.2.10c)$$

$$Z_2 = \hbar\omega_2 + 2\,Z_4 \quad (4.2.10d)$$

$$Z_5 = -kc_{21}c_{11} / [2(c_{12}c_{21} - c_{11}c_{22})^2] \quad (4.2.10e)$$

$$Z_6 = -k\,R\,c_{21} / [\,2\,(c_{12}c_{21} - c_{11}c_{22})\,] \quad (4.2.10f)$$

$$Z_7 = -k\,R\,c_{11} / [\,2\,(c_{12}c_{21} - c_{11}c_{22})\,] \quad (4.2.10g)$$

$$Z_8 = -a\,c_{22} / [\,2\,(c_{11}c_{22} - c_{21}c_{12})\,] \quad (4.2.10h)$$

$$Z_9 = -a\,c_{12} / [\,2\,(c_{11}c_{22} - c_{21}c_{12})\,] \quad (4.2.10i)$$

$$Z_0 = \hbar\omega_1/2 + \hbar\omega_2/2 + Z_3 + Z_4 + k\,R^2/2 + V_0 \quad (4.2.10j)$$

and

$$R = \bar{R}_{bc}^{(s)} - \bar{R}_{bc}^{(d)} \quad (4.2.11a)$$

$$Z = A\,\exp(-a\,\bar{R}_{ab}^{(s)}) \quad (4.2.11b)$$

$$k = 1/2\;\mu_{BC}\,(\omega_{BC}^{(d)})^2. \quad (4.2.11c)$$

The coefficients c_{11}, c_{12}, c_{21} and c_{22}, the distances $R_{bc}^{(d)}$ and $R_{bc}^{(s)}$, the force constant k corresponding to the BC stretch in the excited state, the exponential constants A and a and the normal coordinates q_i are as given in ref.[1]. The time evolution operator in the TDCCM [6-9] is given by,

$$U = \exp\,[S^0\,] \quad (4.2.12a)$$

$$S^0 = \sum_{m,n} s_{mn}\,a_1^{+m}\,a_2^{+n}.$$

The autocorrelation function is given by

$$A(t) = \langle 0,0 \mid U \mid 0,0 \rangle = \exp(s_{00}). \quad (4.2.13)$$

The equations of motion for the cluster amplitudes s are obtained by substituting eq (4.2.12a) and eq.(4.2.12b) in the TDSE and premultiplying both sides of the equation by U and projecting on the eigenstates of the number operators:

$$\langle m,n \mid (iU^{-1}\dot{U} - U^{-1} H U) \mid 0,0\rangle = 0. \tag{4.2.14}$$

The resulting expression is evaluated by the Hausdorff expansion [10) which is shown in detail in Appendix 4.2. Explicitly the working equations are given by

$$\langle p,q \mid i \sum_{m,n} \dot{S}_{mn}\, a_1^{+m}\, a_2^{+n} \mid 0,0 \rangle$$

$$= \langle p,q \mid \{ \sum_{m,n} S_{mn}\, Z_1\, m\, a_1^{+m}\, a_2^{+n} + \sum_{m,n} S_{mn}\, Z_2\, n\, a_1^{+m}\, a_2^{+n}$$

$$+ Z_3\, a_1^{+2} + \sum_{m,n} S_{m+2,n}\, (m+2)(m+1)\, a_1^{+m}\, a_2^{+n}$$

$$+ Z_3 \sum_{m,n,x,y} S_{m-x+2,n-y}\, S_{x-m+2,y-n}\, (m-x+2)\, (x-m+2)\, a_1^{+m}\, a_2^{+n}$$

$$+ Z_4\, a_2^{+2} + Z_4 \sum_{m,n} S_{n,m+2}\, (m+1)(m+2)\, a_2^{+m}\, a_1^{+n}$$

$$+ Z_4\, [\sum_{m,n,x,y} S_{m-x,n-y+2}\, S_{x-m,y-n+2}\, (n-y+2)\, (x-n+2)\, a_1^{+m}\, a_2^{+n}]$$

$$+ Z_5\, a_1^{+}\, a_2^{+} + Z_5 \sum_{m,n} S_{m-1,n+1} (n+1)\, a_1^{+m}\, a_2^{+n}$$

$$+ Z_5 \sum_{m,n} S_{m+1,n-1}\, (m+1)\, a_1^{+m}\, a_2^{+n} + Z_5 \sum_{m,n} S_{mn}\, (m+1)\, (n-1)\, a_1^{+m}\, a_2^{+n}$$

$$+ Z_5 \sum_{m,n,x,y} S_{m-x+1,n-y+1}\, S_{x-m+1,y-n+1}\, [(n-y+1)(x-m+1) +$$

$$(m-x+1)(y-n+1)\,]\, a_1^{+m}\, a_2^{+n} + Z_6\, a_1^{+}$$

$$+ Z_6 \sum_{m,n} S_{m+1,n}\, (m+1)\, a_1^{+m}\, a_2^{+n} + Z_7\, a_2^{+} + Z_7 \sum_{m,n} S_{m,n+1}\, (n+1)\, a_1^{+m}\, a_2^{+n}$$

$$+ A'\, \exp(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n})\, \exp(Z_8 a_1^{+})\, \exp(Z_9 a_2^{+})$$

$$X \sum_{\substack{l,n\\=0}} Y_{ln} \sum_{m=0}^{l} {}^{l}C_m\, Z_8^{l-m}\, a_1^{+m}\, a_2^{+n})\; \} \mid 0,0 \rangle \tag{4.2.15}$$

where

$$Y_{1n} = \sum_{m=n} S_{1m} \, {}^{m}C_{n} \, Z_{9}^{m-n}. \tag{4.2.16}$$

Here $A' = Z \exp(Z_8^2/2 + Z_9^2/2)$ The initial conditions are **s** (0) = 0. The rest of the operators do not contribute as they have the annihilation operators **a** and **a**₋ to the right which give zero when acting on vacuum stale.

4. 2b. Results and Discussion.

We have calculated the autocorrelation functions and spectra for the photodissociation of ICN, BrCN and C1CN. The values of the parameters appearing in the hamiltonian are taken from the work of Beswick and Jortner [1] and are collected in Table 4.2.1. System I corresponds to ICN undergoing direct photodissociation. In addition we have also studied another system corresponding to ICN in the predissociation limit in which the parameter A is reduced to 0.2 X 10 eV (System II). This system was studied earlier by Coalson and Karplus [11]. System III corresponds to BrCN and System IV corresponds to C1CN. The TDCCM calculations were carried at various levels of approximation to the cluster operator S to understand its covergence pattern. Truncations were made such that all s ,0 ≤ m,n < N were included for a given value of N where N is the

TABLE 4.2.2a

SOME S-MATRIX ELEMENTS AT THE END OF 30 FEMTO SECONDS FOR DIFFERENT VALUES OF TRUNCATION INDEX N FOR ICN IN THE PHOTODISSOCIATION LIMIT (SYSTEM I).

	S_{mn}					
N mn	2	3	4	5	6	7
00	-0.1242e+2 [a] -0.2293e+2 [b]	-0.1303e+2 -0.2328e+2	-0.1294e+2 -0.2337e+2	-0.1294e+2 -0.2333e+2	-0.1295e+2 -0.2334e+2	-0.1294e+2 -0.2334e+2
01	0.1228e+1 -0.5147e+0	0.1203e+1 -0.5349e+0	0.1211e+1 -0.5284e+0	0.1208e+1 -0.5306e+0	0.1209e+1 -0.5307e+0	0.1209e+1 0.5300e+0
10	0.3331e+1 0.2004e+1	0.3408e+1 0.2162e+1	0.3339e+1 0.2201e+1	0.3346e+1 0.2173e+1	0.3353e+1 0.2182e+1	0.3348e+1 0.2182e+1
11	0.2444e-2 -0.5445e-1	-0.2635e-2 -0.3965e-1	-0.6781e-2 -0.4831e-1	-0.4236e-2 -0.4612e-1	-0.5572e-2 -0.4628e-1	-0.5009e-2 -0.4679e-1
03		-0.3707e-3 -0.4403e-3	-0.1155e-3 -0.2464e-3	-0.2053e-3 -0.1068e-3	-0.2509e-3 -0.1539e-3	-0.2205e-3 -0.1588e-3
30		0.7904e-2 0.6593e-2	0.6557e-2 0.5732e-2	0.6848e-2 0.5253e-2	0.7183e-2 0.5666e-2	0.6745e-2 0.5579e-2
05				0.4049e-5 0.8121e-5	-0.3855e-5 0.5307e-5	-0.2364e-5 0.4699e-7
50				-0.2171e-4 -0.2616e-4	-0.1124e-4 -0.1863e-4	-0.1336e-4 -0.2104e-4
07						-0.1832e-6 -0.8738e-7
70						0.1502e-6 0.1734e-6

---

a) Real part of S_{mn}.

b) Imaginary part of S_{mn}

TABLE A.2.2b

SOME S-MATRIX ELEMENTS AT THE END OF 30 FEMTO SECONDS FOR DIFFERENT VALUES OF TRUNCATION INDEX N FOR ICN IN THE PREDISSOCIATION LIMIT (SYSTEM II).

	S_{mn}					
N	2	3	4	5	6	7
mn						
00	-0.4327e+1 [a] -0.1381e+2 [b]	-0.4285e+1 -0.1387e+2	-0.4287e+1 -0.1386e+2	-0.4287e+1 -0.1386e+2	-0.4287e+1 -0.1386e+2	-0.4287e+1 -0.1386e+2
01	0.1622e+1 -0.7831e+0	0.1614e+1 -0.7846e+0	0.1614e+1 -0.7846e+0	0.1614e+1 -0.7845e+0	0.1614e+1 -0.7845e+0	0.1614e+1 -0.7845e+0
10	0.1467e+1 0.1707e+1	0.1383e+1 0.1695e+1	0.1392e+1 0.1694e+1	0.1391e+1 0.1695e+1	0.1391e+1 0.1695e+1	0.1391e+1 0.1695e+1
11	0.2126e-3 -0.1322e-1	0.5049e-3 -0.2013e-1	-0.1270e-4 -0.1989e-1	-0.2532e-4 -0.1996e-1	-0.7049e-4 -0.1896e-1	-0.4632e-4 -0.1896e-1
03		-0.7537e-4 -0.3087e-3	-0.1084e-3 -0.3539e-3	-0.1215e-3 -0.3409e-3	-0.1221e-3 -0.3392e-3	-0.1216e-3 -0.3390e-3
30		0.8626e-2 0.4987e-2	0.9384e-2 0.6357e-2	0.8984e-2 0.5578e-2	0.9180e-2 0.5819e-2	0.9100e-2 0.5758e-2
05				-0.8159e-7 -0.7261e-7	-0.1119e-6 -0.2353e-6	-0.9510e-7 -0.1761e-6
50				0.2894e-4 -0.4300e-4	0.3541e-5 -0.2529e-4	0.1187e-4 -0.3782e-4
07						0.8011e-9 0.4376e-9
70						-0.6575e-6 0.5517e-6

a) Real part of S_{mn}.

b) Imaginary part of S_{mn}.

TABLE 4.2.2c

SOME S-MATRIX ELEMENTS AT THE END OF 30 FEMTO SECONDS FOR DIFFERENT VALUES OF TRUNCATION INDEX N FOR BrCN (SYSTEM III).

	S_{mn}					
N mn	2	3	4	5	6	7
00	-0.2441e+2 [a] -0.3080e+2 [b]	-0.2556e+2 -0.3058e+2	-0.2581e+2 -0.3075e+2	-0.2574e+2 -0.3082e+2	-0.2571e+2 -0.3078e+2	-0.2573e+2 -0.3078e+2
01	0.7916e+0 -0.3069e+0	0.7541e+0 -0.2269e+0	0.7526e+0 -0.2373e+0	0.7485e+0 -0.2365e+0	0.7498e+0 -0.2377e+0	0.7502e+0 -0.2372e+0
10	0.4986e+1 0.1948e+1	0.4836e+1 0.1874e+1	0.4910e+1 0.1936e+1	0.4882e+1 0.1957e+1	0.4873e+1 0.1944e+1	0.4881e+1 0.1941e+1
11	-0.4929e-1 -0.4512e-1	-0.1371e-1 -0.4839e-1	-0.1856e-1 -0.4536e-1	-0.1652e-1 -0.4484e-1	-0.1710e-1 -0.4554e-1	-0.1668e-1 -0.4556e-1
03		-0.2745e-3 0.4363e-3	-0.4467e-3 -0.7068e-5	-0.2818e-3 -0.1594e-3	-0.2564e-3 -0.9893e-4	-0.2968e-3 -0.8177e-4
30		0.7066e-2 0.6817e-2	0.[illegible]831e-2 0.5555e-2	0.7169e-2 0.5859e-2	0.6568e-2 0.5759e-2	0.6772e-2 0.5580e-2
05				-0.9155e-5 0.3306e-5	-0.3197e-5 -0.2763e-6	-0.7374e-7 -0.7862e-6
50				-0.1663e-4 -0.8112e-5	-0.5835e-5 -0.7443e-5	-0.1159e-4 -0.6102e-5
07						-0.2195e-6 -0.7341e-7
70						0.5901e-7 0.2316e-7

a) Real part of S_{mn}.

b) Imaginary part of S_{mn}.

TABLE 4.2.1d

SOME S-MATRIX ELEMENTS AT THE END OF 30 FEMTO SECONDS FOR DIFFERENT VALUES OF TRUNCATION INDEX N FOR CICN (SYSTEM IV).

N mn	2	3	4	5	6	7
00	-0.2801e+2 [a] -0.2915e+2 [b]	-0.2815e+2 -0.2893e+2	-0.2841e+2 -0.2895e+2	-0.2640e+2 -0.3004e+2	-0.2937e+2 -0.3004e+2	-0.2937e+2 -0.3002e+2
01	0.3991e+0 -0.1966e+0	0.4520e+0 -0.9755e-1	0.4715e+0 -0.9463e-1	0.4597e+0 -0.8000e-1	0.4589e+0 -0.9168e-1	0.4640e+0 -0.9128e-1
10	0.5322e+1 0.1334e+1	0.4874e+1 0.1447e+1	0.4935e+1 0.1472e+1	0.4923e+1 0.1488e+1	0.4918e+1 0.1494e+1	0.4917e+1 0.1489e+1
11	-0.6834e-1 -0.1900e-1	-0.3048e-1 -0.4001e-1	-0.4111e-1 -0.4211e-1	-0.3534e-1 -0.4727e-1	-0.3812e-1 -0.4431e-1	-0.3920e-1 -0.4489e-1
03		0.6084e-3 -0.1713e-4	-0.4529e-3 -0.1300e-3	-0.4091e-3 -0.4209e-3	-0.3807e-3 -0.2958e-3	-0.4274e-3 -0.1713e-3
30		0.8921e-2 0.6430e-2	0.6804e-2 0.6269e-2	0.7437e-2 0.5312e-2	0.7153e-2 0.5986e-2	0.7208e-2 0.5953e-2
05				0.8369e-5 0.1281e-4	-0.6523e-6 0.2812e-5	-0.5830e-6 0.8029e-7
50				-0.7005e-5 -0.1286e-4	-0.6487e-5 -0.1834e-4	-0.7886e-5 -0.1066e-4
07						0.1831e-6 0.1632e-6
70						-0.1709e-7 -0.1288e-7

a) Real part of S_{mn}.

b) Imaginary part of S_{mn}.

TABLE 4.2.1

Spectroscopic parameters for ABC used in the calculations.

	ω_1 (cm^{-1})	ω_2 (cm^{-1})	$\bar{R}_{CN}^{(s)}$ (A)	$\bar{R}_{IC}^{(s)}$ (A)	$\omega_{CN}^{(d)}$ (cm^{-1})	$\bar{R}_{CN}^{(d)}$ (A)	A (eV)	a (A^{-1})
System I -	499	2207	1.15	2.12	1763	1.2327	0.64(6)	6.68
System II -	499	2207	1.15	2.12	1763	1.2327	0.20(6)	6.68
System III-	580	2187	1.15	1.93	1763	1.2327	0.40(6)	6.68
System IV -	729	2201	1.15	1.76	1763	1.2327	0.15(6)	6.68

[c: The number n in the brackets correspond to multiplication with 10 . The variables are as defined by Beswick and Jortner.]

truncation index. Tables 4.2.2a, 4.2.2b and 4.2.2c show the convergence pattern of a few S-matrix elements for various truncation indices for the four different systems. A good convergence pattern is seen.

The modulus of the autocorrelation functions for different N_s are plotted in Fig. 4.2.1a, b, c and d. As can be seen, the autocorrelation functions obtained by TDCCM are practically indistinguishable from the exact one by about $N_s = 3$ for the direct dissociation. The convergence of the autocorrelation function for ICN is slower in the predissociative System II (Fig. 4.2.1b), but even here, by $N_s = 4$, the TDCCM converges to

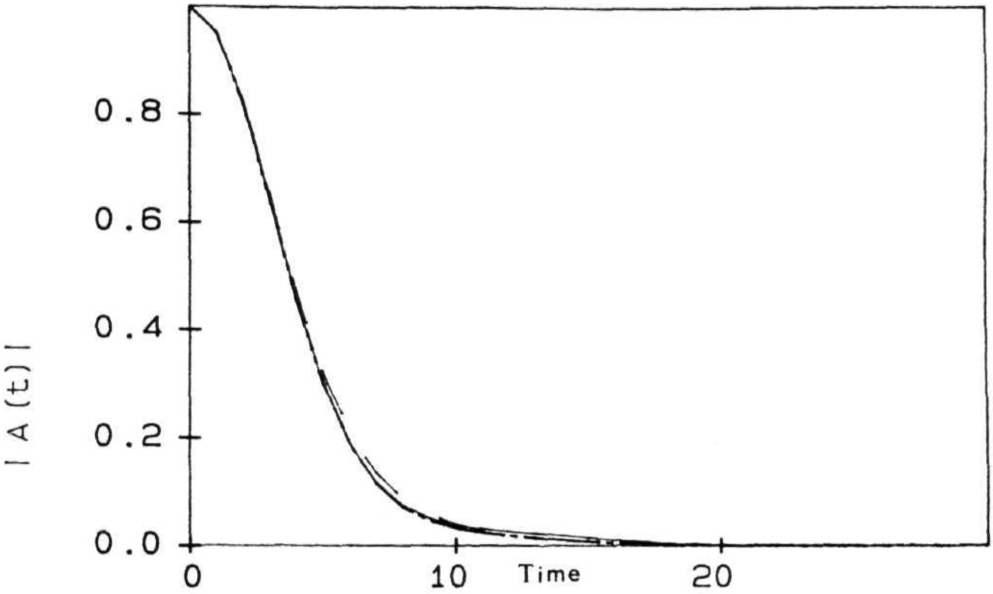


Fig. 4.2.1a: Modulus of the **autocorrelation** function for ICN (System I -photodissociation limit) for various truncation indices. Solid line - basis set expansion, dash and double dot TDCCM at N=7, dash and dot - TDCCM at N=5, long dashes - TDCCM at N=3 and short dashes - TDCCM at N=1.

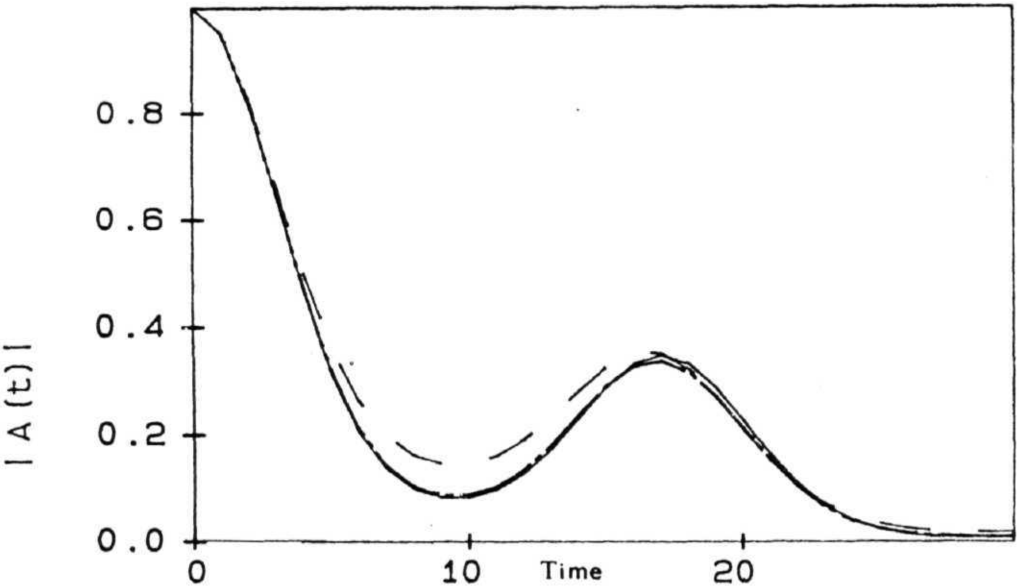


Fig. 4.2.1b: Modulus of the autocorrelation function for ICN (System II -predissociation limit) for various truncation indices. Solid line - basis set expansion, dash and double dot TDCCM at N=7, dash and dot - TDCCM at N=5, long dashes - TDCCM at N=3 and short dashes - TDCCM at N=1.

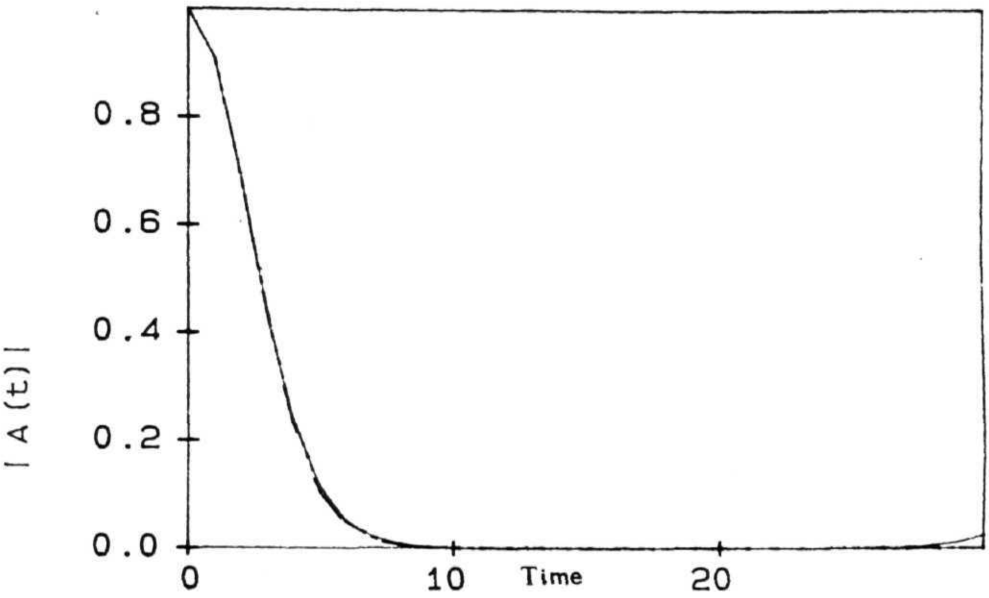


Fig. 4.2.1c: Modulus of the autocorrelation function for BrCN (System III for various truncation indices. Solid line - basis set expansion, dash and double dot - TDCCM at N=7, dash and dot - TDCCM at N = 5, long dashes - TDCCM at N=3 and short dashes - TDCCM at N=1.

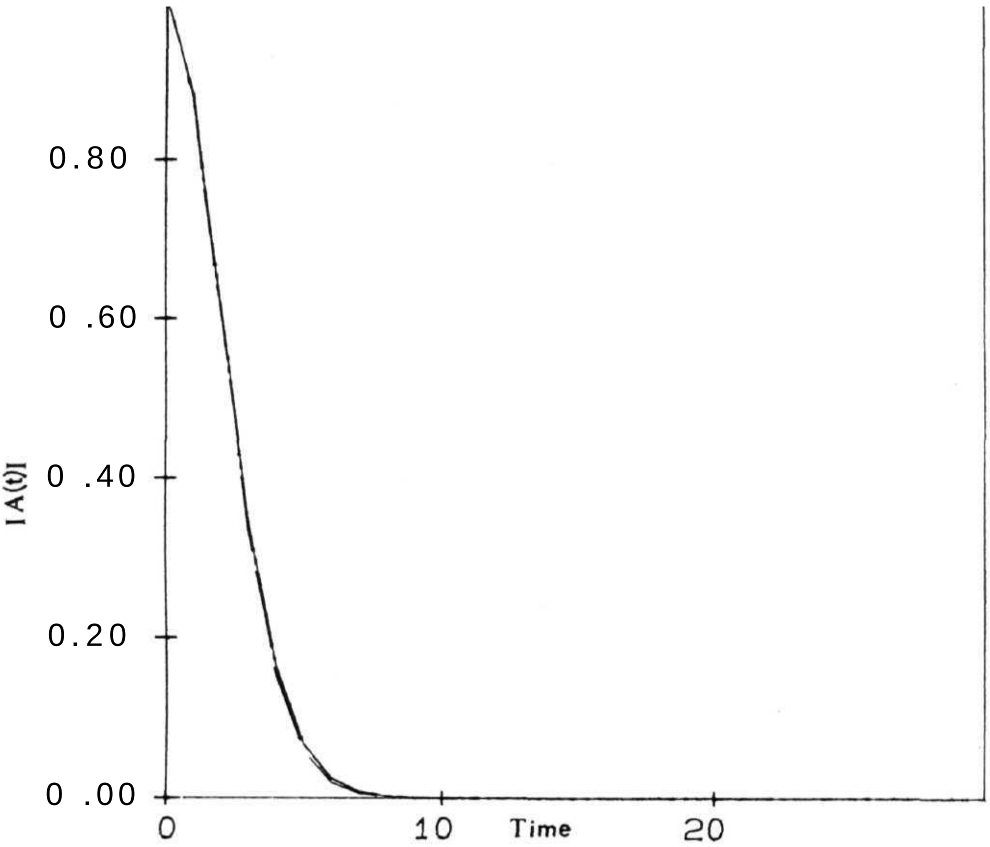


Fig. 4.2.1d: Modulus of the autocorrelation function for C1CN (System IV) for various truncation indices. dash and double dot - TDCCM at N=7, dash and dot - TDCCM at N=5, long dashes - TDCCM at N=3 and short dashes - TDCCM at N=l.

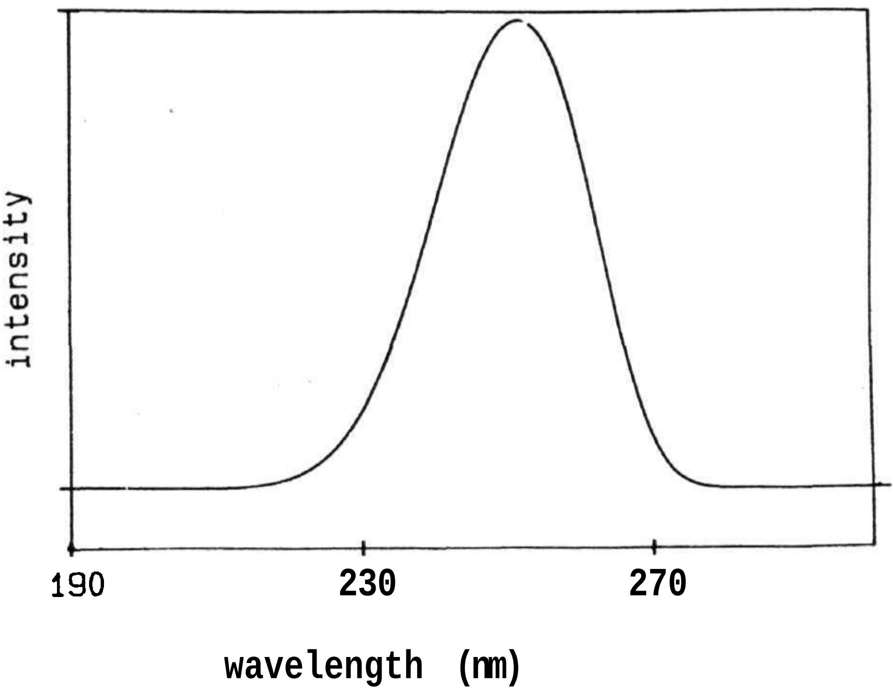


Fig. 4.2.2a: Photodissociation spectrum of ICN (System I) obtained from TDCCM at the truncation index N=7.

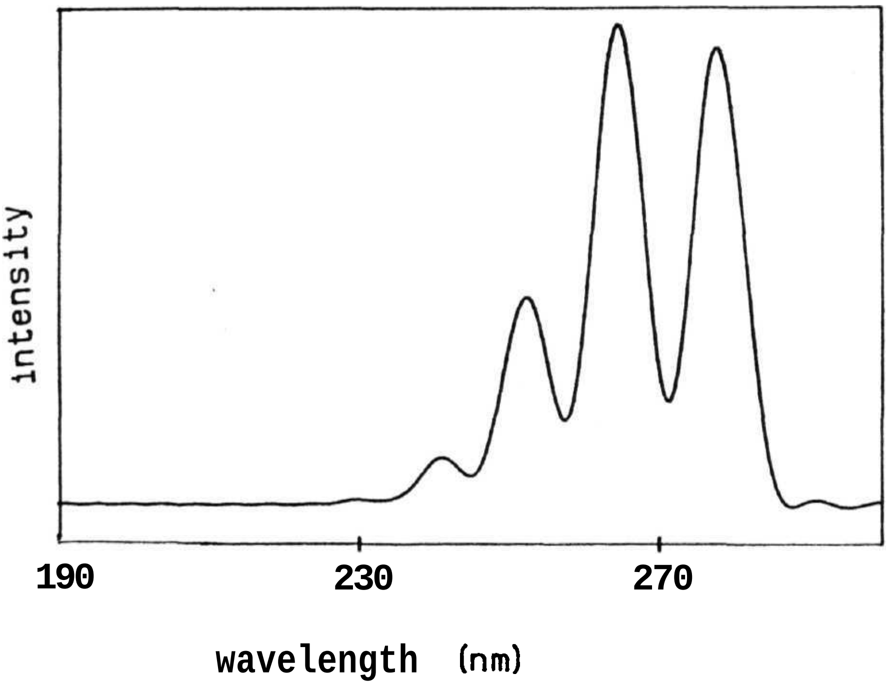


Fig. 4.2.2b: Photodissociation spectrum of ICN (System II) obtained from TDCCM at the truncation index N=7.

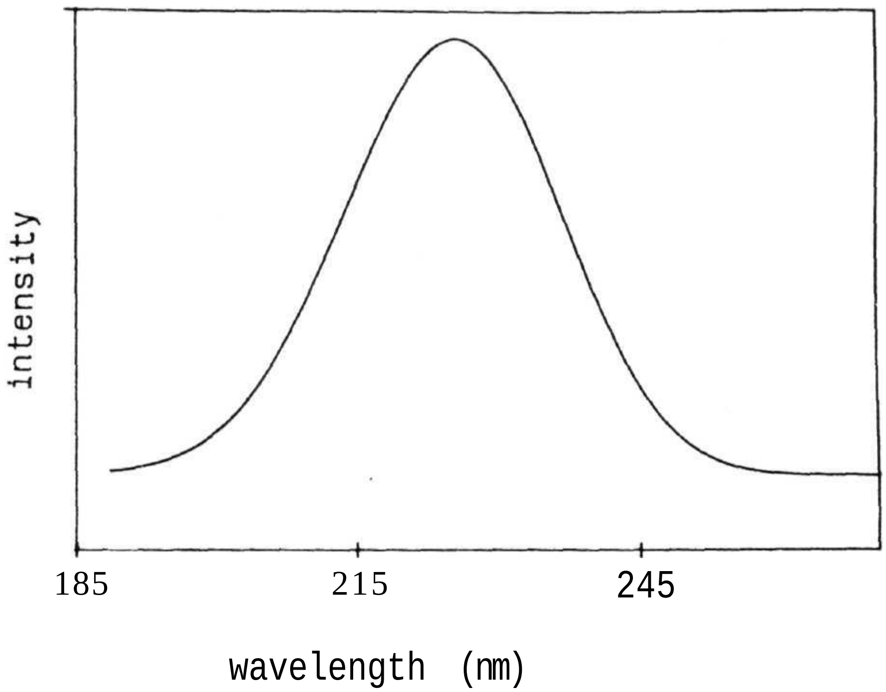


Fig. 4.2.2c: Photodissociation spectrum of BrCN (System III) obtained from TDCCM at the truncation index N=7.

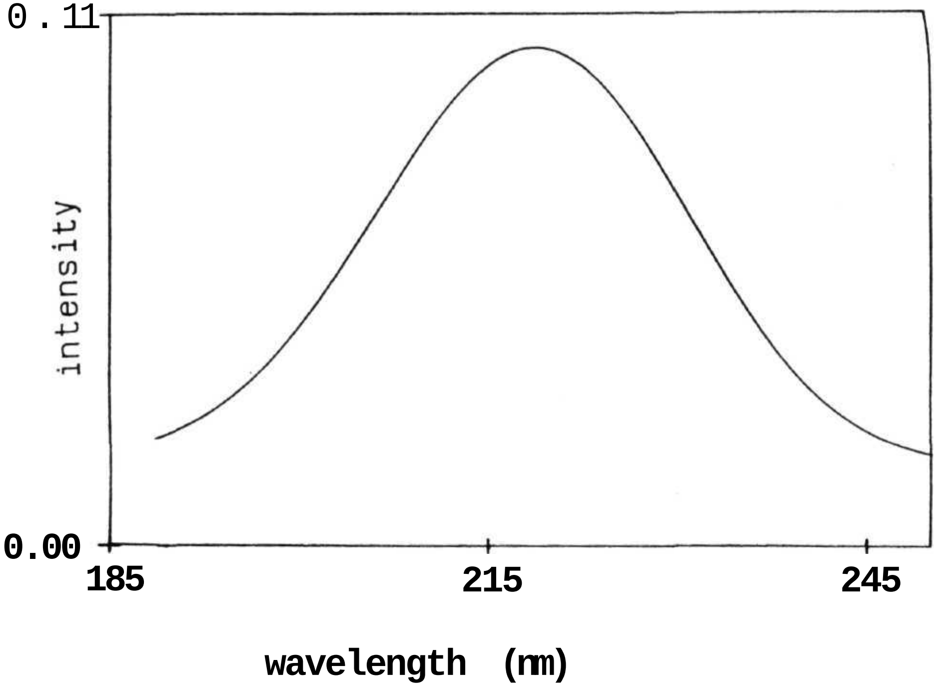


Fig. 4.2.2d: Photodissociation spectrum of C1CN (System IV) obtained from TDCCM at the truncation index N=7.

the exact value. The TDCCM requires 25 variables ([N +1]) at N = 4. On the other hand, the basis set calculations required about 900 functions (30 along each coordinate) for covergence in this coordiate frame. Though non-linear, the TDCCM equations were not stiff and required very little CPU time. The spectra for the systems at $N_s = 7$ are presented in Fig. 4.2.2a, b, c and d.

More recently Coalson and Karplus [11] observed that the variational GWP in the Hartree approximation gave an artificial negative absorption for a two dimensional dissociative surface. While this can be corrected by using dynamical basis sets that move along the classical trajectories [12], the computational requirements once again scale exponentially with the number of degrees of freedom.

4.3. APPLICATION TO HENON - HEILS SYSTEM.

In this section we test the applicability of TDCCM to a two dimensional Henon-Heils system [2]. The conservation of the norm of the wave function is studied.

4.3a. The Model Hamiltonian.

The hamiltonian corresponding to the Henon-Heils potential energy surface is given by

$$H = h(1) + h(2) + \lambda\ (q_2^2\ q_1 + \eta\ q_1^3\ ) \qquad (4.3.1)$$

$$h(i) = -1/2\ \partial^2\ /\partial q_i^2 + 1/2\ \omega_i^2\ q_i^2 \quad ;\ i=1,2. \qquad (4.3.2)$$

The equations of motion for the ground state propagation of the system are obtained similar to the previous section i.e, by solving the TDSE. Converting the **hamiltonian** in terms of boson creation and annihilation operators we obtain

$$H = (a_1^+ a_1 + 1/2) \hbar\omega_1 + (a_2^+ a_2 + 1/2) \hbar\omega_2 + \lambda [(a_2^+ + a_2)^2 (a_1^+ + a_1) + \eta (a_1^+ + a_1)^3]. \qquad (4.3.3a)$$

Rearranging the hamiltonian we obtain

$$H = \bar{\omega}_x a_x^+ a_x + \bar{\omega}_y a_y^+ a_y + A_x(a_x^+ + a_x) + A_y(a_y^+ + a_y) + B_x(a_x^+ a_x^+ + a_x a_x)$$
$$+ B_y (a_y^+ a_y^+ + a_y a_y) + C (a_x^+ a_y^+ + a_x^+ a_y + a_x a_y^+ + a_x a_y) +$$
$$D (a_x^{+2} a_y + 2a_x^+ a_x a_y + a_x^2 a_y + a_x^{+2} a_y + 2a_x^+ a_x a_y^+ + a_x^2 a_y^+) + F \qquad (4.3.3b)$$

where,

$$\bar{\omega}_x = \omega_x + (\hbar/2m\omega_x)\, 2\lambda y_0 \qquad (4.3.3c)$$
$$\bar{\omega}_y = \omega_y \qquad (4.3.3d)$$
$$A_x = (x_0\omega_x^2 + 2\lambda x_0 y_0) \sqrt{\hbar/(2m\omega_x)} \qquad (4.3.3e)$$
$$A_y = (y_0\omega_y^2 + \lambda x_0) \sqrt{\hbar/(2m\omega_y)} + \lambda/ \sqrt{8\omega_x\omega_y} \qquad (4.3.3f)$$
$$B_x = 2\lambda y_0 \hbar/ (4m\omega_x) \qquad (4.3.3g)$$
$$B_y = 0 \qquad (4.3.3h)$$
$$C_{xy} = \lambda x_0 \hbar/ (m \sqrt{\omega_x\omega_y}) \qquad (4.3.3i)$$
$$D = [\lambda\hbar/ (2m\omega_x)] \sqrt{\hbar/(2m\omega_y)} \qquad \mathbf{(4.3.3j)}$$
$$F = \lambda x_0 y_0 + 1/2\, \omega_x x_0 + 1/2\, \omega_y y_0 . \qquad (4.3.3k)$$

The equations of motion are obtained by truncating at N = 1 such that m+n =1 of S_{mn}. This simplifies the evaluation of the norm. The derivation is fairly straightforward and the final equations are

$$i\dot{s}_{00} = A_x s_{10} + A_y s_{01} + B_x s_{10}^2 + B_y s_{01}^2 + 2C_{xy} s_{10} s_{01}$$

$$+ D s_{10}^2 s_{01} + F$$

$$i\dot{s}_{01} = A_y + C_{xy} s_{10} + \bar{\omega}_y s_{01} + D s_{10}^2$$

$$i\dot{s}_{10} = A_x + \bar{\omega}_x s_{10} + C_{xy} s_{01} + 2D s_{10} s_{01}$$

The norm of the wave function is given by

$$\text{Norm} = \exp [s_{10} s_{10}^* + s_{01} s_{01}^* + s_{00} + s_{00}^*].$$

4.3b. Numerical studios.

We have tested the norm of the wave function for two model systems [2]. The parameters are given in Table 4.3.1. The plots of the negative logarithm of the norm vs. time for the two systems are presented in Fig. 4.3.1a and 4.3.1b. For System I (Fig. 4.3.1a), the norm is seen to be conserved for all practical purposes as the values at different times vary by an order of 10 . System II (Fig. 4.3.1b) shows an altogether different behaviour. The norm in this case is seen to be lost. This loss of

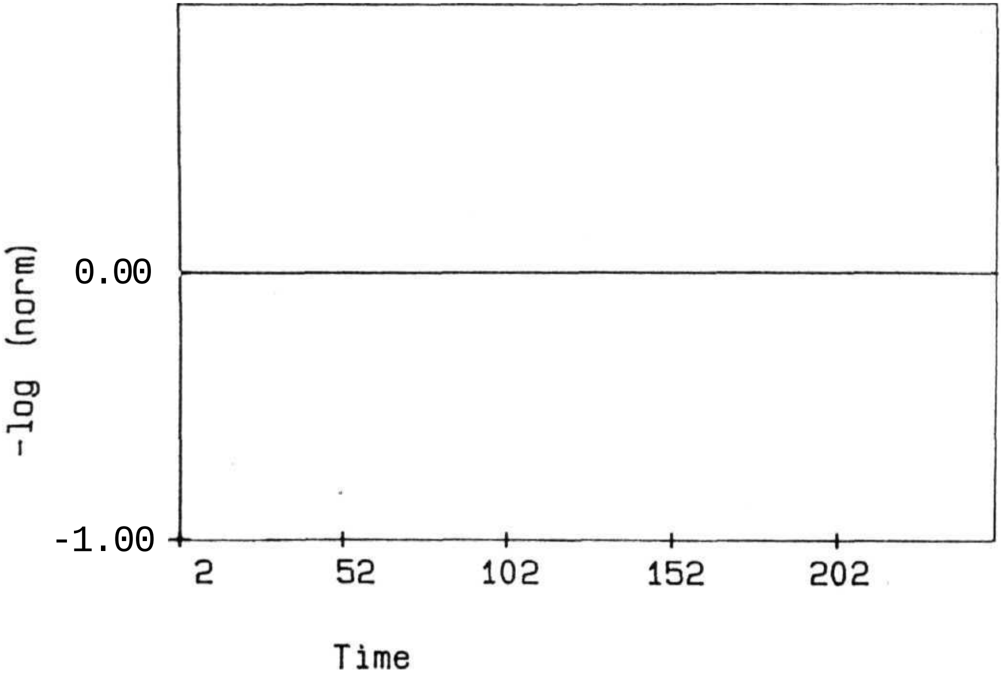


Fig. 4.3.1a: Plot of the logarithm of the norm vs. time for Henon-Heils System I.

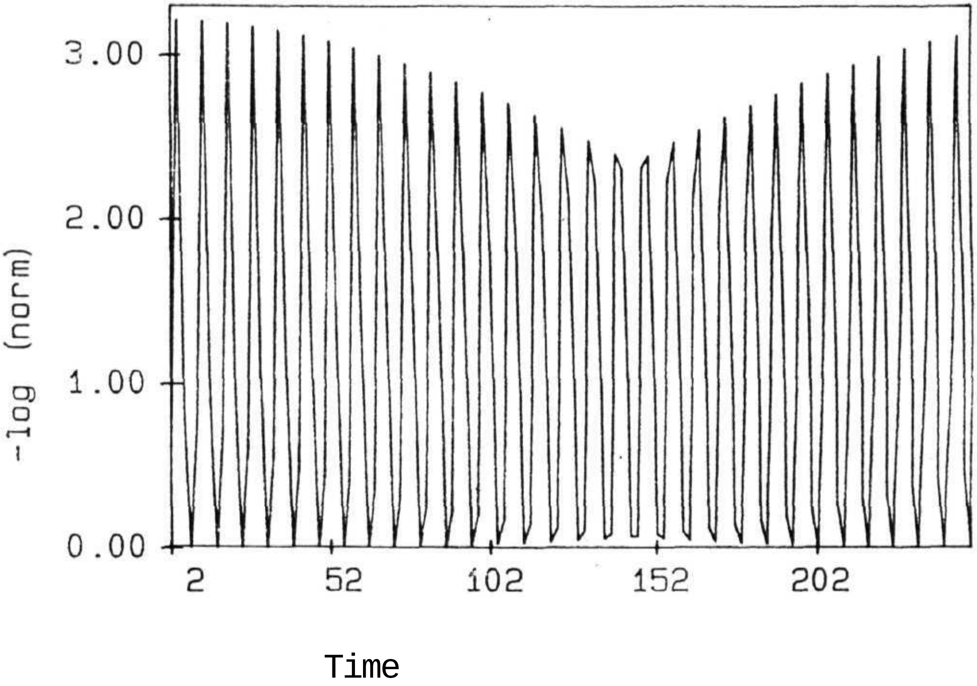


Fig. 4.3.1b: Plot of the logarithm of the norm vs. time for Henon-Heils System II.

norm occurs because the TDCCM approximations can lead to the violation of the hermiticity of the hamiltonian [13]. From chapter 2, the governing equations in the TDCCM approach for the vacuum state propagation is

$$\langle n \mid \bar{H} - iU^{-1}\dot{U} \mid 0 \rangle = 0 \quad \forall n. \qquad (2.2.26a)$$

where

$$\bar{H} = U^{-1}HU \qquad (4.3.6)$$

in any practical calculation, the cluster operator S is truncated to some finite rank. Consequently, all the equations (2.2.26a) are not satisfied. This is equivalent to replacing H with some H. in (2.2.26a) such that

$$\bar{H}_A = \bar{H} - \bar{R} \qquad (4.3.7a)$$

$$\langle n \mid \bar{R} \mid 0\rangle = 0, \quad \text{if } \langle n \mid \bar{H} - iU^{-1}\dot{U} \mid 0\rangle = 0 \qquad (4.3.7b)$$

$$\langle n \mid \bar{R} \mid 0\rangle = \langle n \mid \bar{H} \mid 0 \rangle, \text{ if } \langle n \mid \bar{H} - iU^{-1}\dot{U} \mid 0\rangle \neq 0 \qquad (4.3.7c)$$

If H_A is the hamiltonian from H_A which is generated by the similarity transformation (i.e, $H = U^{-}$ H.U), then the TDCCM solution follows the dynamics generated by H_A. H_A is related to the original hamiltonian through the relation

$$\begin{aligned} H_A &= U \bar{H}_A U^{-1} = U \bar{H} U^{-1} - U \bar{R} U^{-1} \\ &= H - U \bar{R} U^{-1}. \end{aligned} \qquad (4.3.8)$$

If U R U is not hermitian then H. would be non-hermitian. In such a case it could have complex eigenvalues, and, if the wave

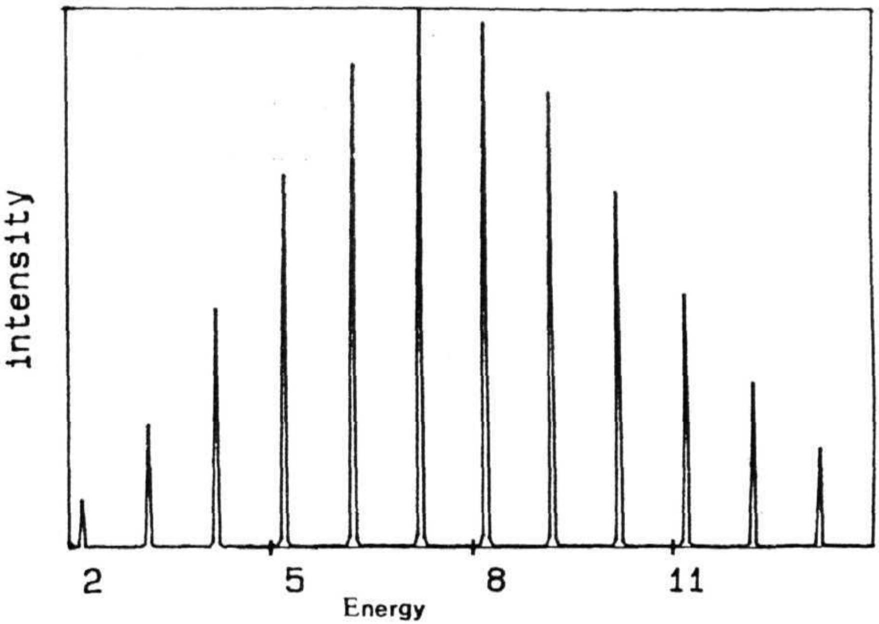


Fig. 4.3.2a: Franck-Condon spectrum of Henon-Heils System I

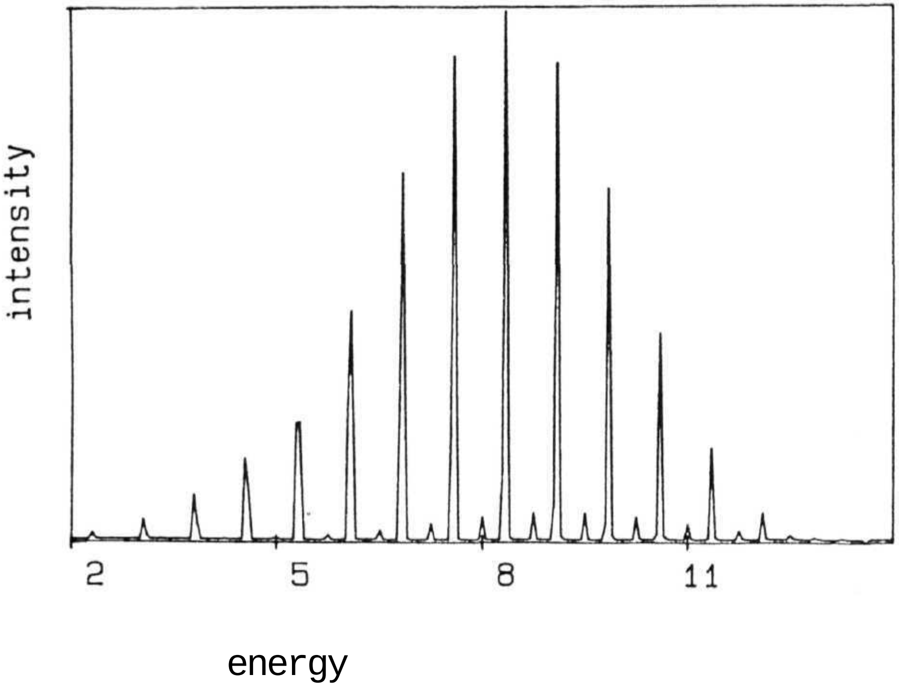


Fig. 4.3.2b: Franck-Condon spectrum of Henon-Heils System II

packet at some stage of its evolution develops a significant overlap with an eigenvector with a complex eigenvalue, it's norm would change. The stronger the anharmonic coupling, the greater is the effect of the R operator since the importance of the higher rank operators increases with the perturbation. This is at the origin of the norm violation, seen oin this case.

The Franck-Condon spectra obtained for the two systems are presented in Fig. 4.3.2a and b. The exact spectra are given in Ref. [2].

TABLE 4.3.1

System	ω_x	ω_y	χ	x_0	y_0
System I	1.1	1.0	-0.11	0.0	4.0
System II	1.1	1.0	-0.11	3.2	3.2

4.4. CONCLUSIONS.

In this chapter we have performed convergence studies of TDCCM by applying it to the two dimensional photodissociation of a few molecules in the Beswick and Jortner model [1]. We have also studied the conservation of norm in TDCCM by applying it to the two dimensional Henon-Heils hamiltonian.

Good convergence pattern of the S-matrix elements is seen in the TDCCM applied to the Beswick and Jortner model hamiltonian. The photodissciation spectra obtained from TDCCM are seen to be in good agreement with the exact spectra. The agreement is not so good in the case of Henon-Heils hamiltonian at S. level of approximation. Here, we also found norm violation. Inclusion of higher rank cluster operators is expected to improve the performance of TDCCM.

On the whole it appears that the TDCCM requires few variables to obtain converged autocorrelation functions. This is to be expected since the approximations in the TDCCM are made to the cluster operator S rather than to the evolution operator U. This effects the convergence of the TDCCM at two levels. For one dimensional systems, the wave function generated by the TDCCM ansatz receives contributions from all the harmonic oscillator eigenstates, even when N_s is finite. This is a consequence of the exponential ansatz. Of course the coefficients of the states whose quantum numbers are larger than N_s would not be independent variables, but would be polynomial functions of the first N_s functions. However, even this improves the flexibility built into the wave function. Thus, fewer number of variables are required to parametrize the TDCCM ansatz than a corresponding basis set expansion. For systems with several degrees of freedom the TDCCM is particularly attractive since the cluster operator is additively seperable. Thus, if the system contains non-interacting subsystems [13], the dynamics of the subgroups can be seperately evaluated and combined additively at the cluster operator level. We believe that our results, though on simple model systems, indicate that this potential of the method realizable.

APPENDIX 4.2.

We describe the procedure to obtain the working equations of motion for the Beswick and Jortner model describing the photodissociation dynamics of molecules in this section, as the potential in this system is a transcendental function. The time dependent Schroedinger equation is given as

$$i\, U^{-1} \dot{U} = U^{-1} H U \tag{A4.1}$$

$$i U^{-1} \dot{U} = \exp(-S)\, H \exp(S) \tag{A4.2}$$

where

$$U = \exp[S]. \tag{A4.3}$$

We will first consider the right hand side of the equation. Each term in the hamiltonian has to be pre and post multiplied by U and U respectively. The similarity transformation is carried out with help of the BCH expansion [10]. We now evaluate the expression term by term.

1st term :

$$\exp(-\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n}) \quad [\, Z_1\, a_1^{+}\, a_1] \quad \exp(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n})$$

$$= Z_1\, a_1^{+}\, a_1 + [\, Z_1 a_1^{+}\, a_1,\ \exp(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n})] +$$

$$1/2!\ [[\, Z_1 a_1^{+}\, a_1,\ \exp(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n})],\ \exp(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n})] + \ldots$$

$$= Z_1\, a_1^{+}\, a_1 + \sum_{m,n} S_{mn}\, Z_1\, m\ a_1^{+m}\, a_2^{+n} \tag{A4.4}$$

2nd Term :

$$\exp(-\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n}) \quad [\, Z_2\, a_2^{+}\, a_2] \quad \exp(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n})$$

This is expanded similar to the 1st term to obtain

$$= Z_2 \, a_2^{+} \, a_2 + \sum_{m,n} S_{mn} \, Z_2 \, n \, a_1^{+m} \, a_2^{+n} \qquad (A4.5)$$

3rd Term

$$= \exp\Big(\sum_{m,n} - S_{mn} \, a_1^{+m} \, a_2^{+n} \Big) \, [\, Z_3 \, a_1^{+2} \,] \, \exp\Big(\sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n} \Big) \qquad (A4.6)$$

As a_1^{+m} commutes with $\exp(\sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n})$ all the commutators in the **Hausdorff** expansion become zero and hence the above expression becomes

$$= Z_3 \, a_1^{+2} \qquad (A4.7)$$

4th Term :

$$= \exp\Big(- \sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n} \Big) \, [Z_3 \, a_1^{2} \,] \, \exp\Big(\sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n} \Big) \qquad (A4.8)$$

Applying the BCH expansion similar to the previous terms we obtain the first commutator as

$$= Z_3 \, \Big[\sum_{m,n} S_{mn} \, 2 \, m \, a_1^{+(m-1)} \, a_1 \, a_2^{+n} + \sum_{m,n} S_{mn} \, m \, (m-1) \, a_1^{+m-2} \, a_2^{+n} \Big]$$

$$(A4.9)$$

The second commutator gives

$$= Z_3 \, \Big[\sum_{m,n} S_{mn} \sum_{x,y} S_{xy} \, m \, x \, a_1^{+(m+x-2)} \, a_2^{+(y+n)} \qquad (A4.10)$$

5th Term :

$$= \exp\Big(- \sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n} \Big) \, [\, Z_4 \, a_2^{+2} \,] \, \exp\Big(\sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n} \Big) \qquad (A4.11)$$

On **the** basis of similar arguments as in the 3rd term evaluation we obtain

$$= Z_4 \, a \qquad (A4.12)$$

6th Term :

$$\exp\left(- \sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right) [Z_4\, a_2^2]\ \exp\left(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right)$$

$$= Z_4 \left[\sum_{m,n} S_{mn}\, 2\, m\, a_2^{+(m-1)}\, a_2\, a_1^{+n} + \sum_{m,n} S_{mn}\, m\, (m-1)\, a_2^{+m-2}\, a_1^{+n} \right]$$

$$+ Z_4 \left[\sum_{m,n} S_{mn} \sum_{x,y} S_{xy}\ m\, x\, a_2^{+(m+x-2)}\, a_1^{+(y+n)} \right] \qquad (A4.13)$$

This is similar to the 4th term.

7th Term :

$$\exp\left(- \sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right) [Z_5\, a_1^{+}\, a_2^{+}]\ \exp\left(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right)$$

$$= Z_5\, a_1^{+}\, a_2^{+} \qquad (A4.14)$$

The rest of the terms follow in asimilar fashion and only the expressions obtained after BCH expansion will be given.

8th Term :

$$\exp\left(- \sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right) [Z_5\, a_2^{+}\, a_1]\ \exp\left(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right)$$

$$= Z_5 \sum_{m,n} S_{mn}\, n\, a_1^{+(m+1)}\, a_2^{+(n-1)} \qquad (A4.15)$$

9th Term :

$$\exp\left(- \sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right) [Z_5\, a_2^{+}\, a_1]\ \exp\left(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right)$$

$$= Z_5 \sum_{m,n} S_{mn}\, m\, a_1^{+(m-1)}\, a_2^{+(n+1)} \qquad (A4.16)$$

10th Term:

$$\exp\left(- \sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right) [Z_5\, a_1 a_2]\ \exp\left(\sum_{m,n} S_{mn}\, a_1^{+m}\, a_2^{+n} \right)$$

$$= Z_5 \sum_{m,n} S_{mn}\, m\, n\, a_1^{+(m-1)}\, a_2^{+(n+1)} +$$

$$Z_5 \sum_{m,n,x,y} S_{mn} S_{x,y} \quad (nx+my) \quad a_1^{+(m-1+x)} \; a_2^{+(n-1+y)} \tag{A4.17}$$

11th Term:

$$\exp(-\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n}) \; [\; Z_6 \, a_1^{+} \;] \; \exp(\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n})$$

$$= Z_6 \, a_1^{+} \tag{A4.18}$$

12th Term:

$$\exp(-\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n}) \; [Z_6 \, a_1] \; \exp(\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n})$$

$$= Z_6 \sum_{m,n} S_{mn} \, m \, a_1^{+(m-1)} \; a_2^{+n} \tag{A4.19}$$

13th Term:

$$\exp(-\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n}) \; [\; Z_7 \, a_2^{+} \;] \; \exp(\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n})$$

$$= Z_7 \, a_2^{+} \tag{A4.20}$$

14th Term:

$$\exp(-\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n}) \; [\; Z_7 \, a_2 \;] \; \exp(\sum_{m,n} S_{mn} a_1^{+m} a_2^{+n})$$

$$= Z_7 \sum_{m,n} S_{mn} \, n \, a_1^{+m} \; a_2^{+(n-1)} \tag{A4.21}$$

We now consider the last **term** of the **hamiltonian** i.e, the exponential part of the potential energy surface which is given by

$$Z \exp [\; Z_8 \; (\; a_1^{+} + a_1) + Z_9 \; (\; a_2^{+} + a_2 \;) \;]. \tag{A4.22}$$

In general, an exponential of the **linear** combination of any two elements whose commutator commutes with each of these elements can be written as [10]

$$\exp [\; T \; (\; a^{+} + a \;)] = \exp(T^2/2) \; \exp(Ta^{+}) \; \exp(Ta) \tag{A4.23}$$

where T is a constant. Hence the last term in the hamiltonian can be written as

$$= A' \quad \exp(Z_8 a_1^{+}) \; \exp(Z_8 a_1) \; \exp(Z_9 a_2^{+}) \; \exp(Z_9 a_2) \qquad (A4.24)$$

where,

$$A' = Z \exp\,(Z_8^2\;/2) \; \exp(Z_9^2\;/2) \qquad (A4.25)$$

We now perform similarity transformation on this part of the hamiltonian.

$$\exp(-S) \; [\; A' \; \exp(Z_8 a_1^{+}) \; \exp(Z_8 a_1) \; \exp(Z_9 a_2^{+}) \; \exp(Z_9 a_2)] \; \exp(S)$$

$$= \exp(-\sum_{m,n} S_{mn} \; a_1^{+m} \; a_2^{+n} \;) \; [\; A' \exp(Z_8 a_1^{+}) \; \exp(Z_8 a_1) \; \exp(Z_9 a_2^{+}) \; \exp(Z_9 a_2)]$$

$$X \quad \exp(\sum_{m,n} S_{mn} \; a_1^{+m} \; a_2^{+n} \;)$$

$$= A' \; \exp(\sum_{m,n} S_{mn} \; a_1^{+m} \; a_2^{+n} \;) \; \exp(Z_8 a_1^{+}) \; \exp(Z_8 a_1) \; \exp(Z_9 a_2^{+}) \; \exp(Z_9 a_2)$$

$$X \quad \exp(\sum_{m,n} S_{mn} \; a_1^{+m} \; a_2^{+n} \;) \quad \exp(-Z_9 \; a_2) \; \exp(Z_9 \; a_2) \qquad (A4.26)$$

The BCH expansion is applied to the following part of the above equation,

$$\exp(Z_9 \; a_2) \; \exp(\sum_{m,n} S_{mn} \; a_1^{+m} \; a_2^{+n} \;) \; \exp(-Z_9 \; a_2)$$

We now obtain the following equation

$$\exp(Z_9\ a_2)\ \exp(\sum_{m,n} S_{mn}\ a_1^{+m}\ a_2^{+n}\ )\ \exp(-Z_9\ a_2)$$

$$= \sum_{\substack{l,n\\=0}} S_{ln} \quad \sum_{m=0}^{n} {}^{n}C_m\ Z_9^{n-m}\ a_1^{+l}\ a_2^{+m}\ ) \qquad \text{(A4.27)}$$

Substituting the above expression in eq. (A4.26) we obtain

$$= \quad A'\ \exp(\sum_{m,n} S_{mn}\ a_1^{+m}\ a_2^{+n}\ )\ \exp(Z_8 a_1^{+})\ \exp(Z_9 a_2^{+})\ \exp(Z_8 a_1)$$

$$\times \quad \sum_{\substack{l,n\\=0}} S_{ln} \quad \sum_{m=0}^{n} {}^{n}C_m\ Z_9^{n-m}\ a_1^{+l}\ a_2^{+m}\ )\ \exp(\ Z_9 a_2). \qquad \text{(A4.28)}$$

This equation can be rewritten as

$$A'\ \exp(\sum_{m,n} S_{mn}\ a_1^{+m}\ a_2^{+n}\ )\ \exp(Z_8 a_1^{+})\ \exp(Z_9 a_2^{+})\ \exp(Z_8 a_1)$$

$$\times \quad \sum_{\substack{l,n\\=0}} S_{ln} \quad \sum_{m=0}^{n} {}^{n}C_m\ Z_9^{n-m}\ a_1^{+l}\ a_2^{+m}\ )\ \exp(-Z_8 a_1)\ \exp(Z_8 a_1)\ \exp(\ Z_9 a_2).$$

$$\text{(A4.29)}$$

Consider the following part of the above equation •

$$\exp(Z_8 a_1) \quad \sum_{\substack{l,n\\=0}} S_{ln} \quad \sum_{m=0}^{n} {}^{n}C_m\ Z_9^{n-m}\ a_1^{+l}\ a_2^{+m}\ )\ \exp(-Z_8 a_1).$$

Substituting

$$\sum_{\substack{l,n\\=0}} S_{ln} \quad \sum_{m=0}^{n} {}^{n}C_m\ Z_9^{n-m}\ a_1^{+l}\ a_2^{+m}\ ) \qquad = \sum_{l,m} Y_{lm}\ a_1^{+l}\ a_2^{+m} \qquad \text{(A4.30)}$$

we obtain

$$\exp(Z_8 a_1) \quad \sum_{\substack{l,n\\=0}} S_{ln} \quad \sum_{m=0}^{n} {}^{n}C_m \; Z_9^{n-m} \; a_1^{+l} \; a_2^{+m} \;) \; \exp(-Z_8 a_1)$$

$$= \exp(Z_8 a_1) \; [\sum_{l,m} Y_{lm} \; a_1^{+l} \; a_2^{+m} \;] \; \exp(-Z_8 a_1). \qquad \text{(A4.31)}$$

Applying the **BCH** expansion again on the RHS of the above equation we **obtain**,

$$\exp(Z_8 a_1) \; [\sum_{l,m} Y_{lm} \; a_1^{+l} \; a_2^{+m} \;] \; \exp(-Z_8 a_1)$$

$$= \quad \sum_{\substack{l,n\\=0}} Y_{ln} \quad \sum_{m=0}^{l} {}^{l}C_m \; Z_8^{l-m} \; a_1^{+m} \; a_2^{+l} \;). \qquad \text{(A4.32)}$$

Substituting the above equation in eq.(A4.29) we obtain

$$A' \quad \exp(\sum_{m,n} S_{mn} \; a_1^{+m} \; a_2^{+n} \;) \; \exp(Z_8 a_1^{+}) \; \exp(Z_9 a_2^{+})$$

$$X \qquad \sum_{\substack{l,n\\=0}} Y_{ln} \quad \sum_{m=0}^{l} {}^{l}C_m \; Z_8^{l-m} \; a_1^{+m} \; a_2^{+l} \;) \; \exp(Z_8 a_1) \; \exp(Z_9 a_2).$$

(A4.33)

This expression being in the normal order can be easily applied to the ground state propagation. The RHS of the TDSE is now completely written for the ground state propagation as

$$U^{-1} \; H \; U = \quad \sum_{m,n} S_{mn} \; Z_1 \; m \quad a_1^{+m} \; a_2^{+n} + \quad \sum_{m,n} S_{mn} \; Z_2 \; n \; a_1^{+m} \; a_2^{+n}$$

$$+ \; Z_3 \; a_1^{+2} + \; \sum_{m,n} S_{mn} \; m \; (m-1) \; a_1^{+m-2} \; a_2^{+n} \;]$$

$$+ \; Z_3 \; [\; \sum_{m,n} S_{mn} \; \sum_{x,y} S_{xy} \quad m \; x \; a_1^{+(m+x-2)} \; a_2^{+(y+n)} \; + \; Z_4 \; a_2^{+2}$$

$$+ \; Z_4 \; \sum_{m,n} S_{mn} \; m \; (m-1) \; a_2^{+m-2} \; a_1^{+n} \;] \; + \; Z_4 \; [\; \sum_{m,n} S_{mn} \; \sum_{x,y} S_{xy} \quad m \; x$$

$$a_2^{+(m+x-2)} \; a_1^{+(y+n)}] + Z_5 \, a_1^{+} a_2^{+} + Z_5 \sum_{m,n} S_{mn} \, n \, a_1^{+(m+1)} \, a_2^{+(n-1)}$$

$$+ Z_5 \sum_{m,n} S_{mn} \, m \; a_1^{+(m-1)} \, a_2^{+(n+1)} + Z_5 \sum_{m,n} S_{mn} \, m \, n \, a_1^{+(m-1)} \, a_2^{+(n+1)} +$$

$$Z_5 \sum_{m,n,x,y} S_{mn} \, S_{xy} \; (nx+my) \; a_1^{+(m-1+x)} \; a_2^{+(n-1+y)} + Z_6 \, a_1^{+}$$

$$+ Z_6 \sum_{m,n} S_{mn} \, m \, a_1^{+(m-1)} \, a_2^{+n} + Z_7 \, a_2^{+} + Z_7 \sum_{m,n} S_{mn} \, n \, a_1^{+m} \, a_2^{+(n-1)}$$

$$+ \; A' \exp(\sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n}) \exp(Z_8 a_1^{+}) \exp(Z_9 a_2^{+})$$

$$X \sum_{\substack{l,n \\ =0}} Y_{ln} \sum_{m=0}^{l} {}^{l}C_m \, Z_8^{l-m} \, a_1^{+m} \, a_2^{+l} \;) \exp(Z_8 a_1) \exp(Z_9 a_2).$$

(A4.34)

Considering the LHS of the TDSE we obtain,

$$iU^{-1} \dot{U} = i \exp(- \sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n}) \, [\partial / \partial t] \, \exp(\sum_{m,n} S_{mn} \, a_1^{+m} \, a_2^{+n})$$

$$= i \sum_{m,n} \dot{S}_{mn} \, a_1^{+m} \, a_2^{+n}.$$

CA4.35)

Equating the identical powers of **a** and **a**~ we obtain the equations of motion which are integrated to obtain the S 's (structure constants).

REFERENCES

1. a) J. A. Beswick and J. Jortner, Chem. Phys. 24, 1 (1977); b) 0. Atabek, J. A. Beswick, R. Lefebvre, S. Mukamel and J. Jortner , J. Chem. Phys. 65, 4035 (1976); c) idem, Chem. Phys. Lett. 46, 211 (1977); d) R. C. Brown and E. J. Heller, J. Chem Phys 75, 186 (1981).
2. E. J. Heller, J. Chem. Phys., 75, 2923 (1981).
3. L. A. Gribov and W. J. Orville Thomas, Theory and methods of calculation of molecular sectra, (John Wiley, New York), (1988).
4. a) E. J. Heller, J. Chem. Phys. 62, 1544 (1975);b) S.Y.Lee and E. J. Heller,c) idem, J. Chem. Phys. 76,3035 (1982);d) E. J. Heller, Acc. Chem. Res. 14, 368 (1981);e) A. Warshel and J.K. Hwang, J. Chem. Phys. 82, 1756 (1985);f) J. K. Hwang and A. Warshel, Chem. Phys. Lett. 115, 281 (1985).
5. G. Herzberg, Spectra of diatomic molecules (Van Nostrund, New York) (1950); M. Shapiro and R. D. Levine, Chem. phys. Lett. 5, 499 (1970); C. E. Kaplan and M. S. Child, Mol. Phys. 23, 249 (1972); M. Gebelein and J. Jortner, Theor. Chim. Acta. 25, 143 (1972); M. Shapiro, J. Chem. Phys., 56, 2582 (1972); S. Mukamel and J. Jortner, J. Chem. Phys., 60, 4760 (1974); Y. Band and K. Freed, J. Chem. Phys. 64, 4329 (1976); R. Schinke, J. Chem. Phys. 92 (1990) 2397; R. Schinke, M. Nonella., H. U. Suter and J. R. Huber, J. Chem. Phys. 93, 1098 (1990); P. G. Harper and J. Pfab, Mol. Phys., 78, 1337 (1993). J. P. Simons, J. Phys. Chem., 88, 2594 (1984).

6. J. Arponen, Ann. Phys., **151**, 311 (1983); J. Arponen and E. Pajanne 1989, Lecture notes in chemistry, Vol. 50, edited by Mukherjee D. p. 79 (Springer, Berlin);

7. M. Durga Prasad, J. Chem. Phys., 88, 7005 (1988);

8. S. Guha and D. Mukherjee, Chem. Phys. Lett. 186, 84 (1991).

9. G. Madhavi Sastry and M. Durga Prasad, Theor. Chim. Acta. (submitted for publication).

10. R. M. Wilcox, J. Math. Phys. 8, 962 (1967).

11. R. D. Colason and M. Karplus, J. Chem. Phys.,93, 3919 (1990).

12. J. Kucar and H. D. Meyer, J. Chem. Phys., 90, 5566 (1989); R.D. Coalson and M. Karplus, Chem. Phys.Lett. 90, 301 (1983) ; D. Hsu and D. F. Coker, J. Chem. Phys. 96, 4266 (1992) E.S. Hernandez and D. M. Jezek, Phys. Rev. A 38, 4455 (1988).

13. M. Durga Prasad, Lecture notes in chemistry, Vol. 50, edited by Mukherjee D. p. 321 (Springer, Berlin).

CHAPTER 5

LIE-ALGEBERAIC STUDIES OF NON-ADIABATIC DYNAMICS

5.1. INTRODUCTION

In this chapter, we specifically study the applicability of the quadratic Lie-algebraic approach (1,2) and the time dependent coupled cluster method (TDCCM) [3-5] to non-adiabatic dynamics within the framework of the linear coupling model [6].

Chemical phenomena such as the unimolecular and electron transfer reactions, non-radiative transitions, etc. are influenced by the non-adiabatic dynamics of the system [6-9]. Various methods have been applied to obtain the non-adiabatic dynamics of a system. These methods can be catogorised as the time independent and the time dependent methods. The time independent approach is based on the Ritz variational principle in which the hamiltonian matrix is constructed in a basis formed by the product functions of the electronic and vibrational states of the uncoupled system [10-20]. This hamiltonian matrix is diagonalised to obtain the eigenvalues and eigenvectors. The major drawback of these methods is that the number of basis functions required for a system consisting of d degrees of freedom is proportional to N where N is the typical number of the basis functions for a one degree freedom problem leading to an exponential increase in the computational effort. Hence, alternative methods are desirable to calculate the dynamics of these systems. The time dependent methods involve the application of time dependent perturbation theory (in which the non-adiabatic coupling is treated as the perturbation) [21] or the semiclassical methods such as the gaussian wave packet approach (GWP) [22-26] (in which the wave packet is a travelling gaussian and the potential is expanded at the centroid of the wave packet), and the time dependent self consistent field method (TDSCF) [27-291. The time dependent perturbation theory breaks down for strong coupling strengths and for long time dynamics. The GWP cannot account for the anharmonicities prevailent in the system and ultimately it has to be improved further by using the conventional basis set expansion or perturbation theory. Similarly the TDSCF deviates from the exact dynamics at long times and requires CI for numerical convergence. It is against this background that we undertake our studies of the algebraic approaches to non-adiabatic dynamics.

In all our applications in this chapter, we assume that only two electronic states belonging to different irreducible representations of the molecular point group and n vibrational modes, are relevant to the dynamics. We assume that the relevant hamiltonian can be written as [6]

$$H = \sum_i |e_i\rangle \epsilon_i \langle e_i| + \sum_n \omega_n a_n^+ a_n + \sum_{i,j,n} |e_i\rangle [V_n^{(ij)} (a_n^+ + a_n)] \langle e_j| . \tag{5.1.1}$$

Here $|e_i\rangle$'s are the electronic states and a_n and a_n are the usual boson ladder operators of the nth vibrational mode. This hamiltonian has been extensively studied in the past and is found to be adequate for a large number of systems [6J. The wave function for such systems is given by

$$\psi = \sum_i | e_i\rangle \phi_i (R,t) \tag{5.1.2}$$

where ϕ are the vibrational wave functions associated with the ith electronic state.

In the matrix representation the vibrational wave function can be written as

$$\phi = \begin{pmatrix} \phi_1 \ (R) \\ \phi_2 \ (R) \end{pmatrix} \qquad 5.1.3)$$

The $\phi_i(R)$ are vibrational wave packets moving on different surfaces. They have different momenta and centroids. To obtain the equations of motion by the gaussian wave packet propagation approach (GWP) [22-26] in which the potential is expanded as a Taylor series at the centroid of the wave packet, chosing the point around which the potential is to be expanded becomes a problem as both the nuclear wave functions ϕ_1 and ϕ_2 corresponding to the two electronic states have different centroids in general, Second, if any one of the ϕ_i are equal to zero, the exponent γ in the gaussian ansatz for ϕ_i should be equal to -∞. Representing this logarithmic singularity is difficult in practice. We have circumvented this problem by mapping the hamiltonian (eq.(5.1.1)) on to a purely vibrational hamiltonian confined to a single electronic surface. The details of the mapping for the one-dimensional case are presented in Sec. 5.2a. In Sec. 5.2b we extend it to the multidimensional case. The application of the quadratic Lie-algebraic approach to this hamiltonian is described in Sec. 5.2c. In section 5.2d, we present the numerical calculations for some one and two dimensional model systems. Application of TDCCM to obtain the dynamics of the mapped hamiltonian is dicussed in Sec. 5.2e. In Sec. 5.3 and 5.4 we apply the multireference TDCCM to the original unmapped **hamiltonian** (eq. 5.1.1) involving the electronic degree of freedom explicitly.

5.2. MAPPED HAMILTONIAN APPROACH.

In this section, we discuss the mapping of the **multisurface** hamiltonian (eq. (5.1.1)) of a system specifically consisting of two electronic surfaces belonging to different irreducible **representations** of the molecular point group, on to a single surface hamiltonian. We first consider a situation where only one vibrational mode (the coupling mode) is relevant to the dynamics and describe the mapping. We then extend it to the n vibrational mode problem.

5.2a. The Mapped **Hamiltonian** for single mode systems.

The hamiltonian for the single mode case is given by

$$H = \sum_{i} |e_i\rangle \, \varepsilon_i \, \langle e_i| + \omega_c \, a_c^{+} a_c + \sum_{i \neq j} |e_i\rangle \left[V_c^{ij} \left(a_c^{+} + a_c \right) \right] \langle e_j| \tag{5.2.1}$$

The subscript c indicates here and in the following, that the normal coordinate is a **coupling** mode. Because the two states belong to different irreducible **representations**, the coupling coordinate is always **non-totally** symmetric and hence cannot have intrastate coupling. We take the zero of energy to be the midpoint of the two electronic states such that, ε = $-c$ and ε = ε where 2 ε is the energy gap between the two states at the equilibrium geometry of the ground state.

Let us now analyse the structure of the **Hilbert** space $\mathbb{H}_s$ relevant to the dynamics of this system. This Hilbert space is formed by the **direct** product of the **Hilbert** spaces of the electronic and vibrational sub-systems.

$$\mathbb{H}_s = \mathbb{H}_e \otimes \mathbb{H}_v \tag{5.2.2a}$$

$$\mathbb{H}_e = \{ |e_1\rangle , |e_2\rangle \} \tag{5.2.2b}$$

$$\mathbb{H}_v = \{ \phi_n (q) ; 0 \leq n \leq \infty \}. \tag{5.2.2c}$$

Here ϕ are the harmonic oscillator **eigenfunctions**. Let $|e.\rangle$ and $|e_2\rangle$ belong to the irreducible **representations** Γ and Γ_2 **respectively**. Since the **hamiltonian** must always transform as the totally symmetric **representation**, the coupling **mode** belongs to Γ_c = r. $\otimes \Gamma$ Consequently, all the elements in $\mathbb{H}$ belong to either the totally symmetric **representation** **(when n** is even) or to the **r** **representation** (when n is odd). Thus, the elements in $\mathbb{H}$ belong either to r (when the electronic state is $|e_1\rangle$ and the vibrational quantum number is even or when the electronic state is $|e_2\rangle$ and the vibrational quantum number is odd since r $\otimes \Gamma$ = Γ) or to Γ (in the opposite cases). **Symbolically**, this can be written as

$$\mathbb{H}_s = \mathbb{H}_1 \cup \mathbb{H}_2 \tag{5.2.3a}$$

$$\mathbb{H}_1 = \{ |e_i\rangle \phi_n \quad ; i=1 \text{ and } n \text{ even or } i=2 \text{ and } n \text{ odd}) \tag{5.2.3b}$$

$$\mathbb{H}_2 = \{ |e_i\rangle \phi_n \quad ; i=1 \text{ and } n \text{ odd or } i=2 \text{ and } n \text{ even}). \tag{5.2.3c}$$

Since the hamiltonian cannot couple elements belonging to different symmetries, a wave packet initially started in one of the two subspaces ($\mathbb{H}_1$ or $\mathbb{H}_2$) would continue to evolve within that subspace. Thus, for such initial conditions it is sufficient to expand the wave packet in terms of the basis functions of either $\mathbb{H}_1$ or $\mathbb{H}_2$. We now note that the number of elements in $\mathbb{H}_1$ (or $\mathbb{H}_2$) is identical to the number of elements in H and hence it is possible to define a one-to-one correspondence between these two subspaces.

$$\mathbb{H}_V \longleftrightarrow \mathbb{H}_1 \qquad (5.2.4a)$$

$$\phi_n \longleftrightarrow \phi_n |e_i\rangle \qquad (5.2.4b)$$

The correspondence is completely defined when the electronic state index i is uniquely defined for a given n. In case of $\mathbb{H}$ the electronic state is e_1 (i=l) whenever n is even and e_2 whenever n is odd. The opposite holds in case of $\mathbb{H}$ With this identification, the mapping between $\mathbb{H}$ and $\mathbb{H}$ is complete.

In the next step, we construct a model hamiltonian $\mathbb{H}$ whose matrix elements in $\mathbb{H}$ are identical to the matrix of H in IH For the first term in H ($\omega a^\dagger a$), the matrix elements in $\mathbb{H}$ are $\langle e_1 \phi_m | \omega a_i^\dagger a_i | e_j \phi_n \rangle = m\omega\, \delta_{mn}\, \delta_{ij}$ The corresponding term in $\mathbb{H}_1$ is then simply $\omega_c a_c^\dagger a_c$. For the second term ($\sum_i \epsilon_i |e_i\rangle\langle e_i|$) the matrix elements are

$$\langle e_i\, \phi_m | \sum \epsilon_R\, |e_R\rangle\langle e_R| \; |e_j\, \phi_n\rangle = \epsilon_i\, \delta_{ij}\, \delta_{mn} \qquad \textbf{(5.2.5)}$$

Recalling that $s.$ are $+ s$ depending upon whether m is even or odd we find that the term in H_1 is $-\epsilon \cos(n\, a_c^+ a_c)$ since

$$\langle \phi_m | \cos (\pi\, a_c^+ a_c) | \phi_n \rangle = \langle \phi_m | \cos (n \pi) | \phi_n \rangle \tag{5.2.6a}$$

$$= (-1)^m \delta_{mn} . \tag{5.2.6b}$$

Finally, the last term in the hamiltonian ($\sum |e_i\rangle V_c^{ij} (a_c^+ + a_c) \langle e_j|$) maps on to $V_c\,(a_c^+ + a_c)$. With this, the model hamiltonian $\overline{H}_1$ can be written as

$$\overline{H}_1 = \omega_c\, a_c^+ a_c - \epsilon \cos (\pi\, a_c^+ a_c) + V_c (a_c^+ + a_c) . \tag{5.2.7a}$$

Similarly, for $\mathbb{H}$ one can show that

$$\overline{H}_2 = \omega_c\, a_c^+ a_c + \epsilon \cos (\pi\, a_c^+ a_c) + V_c\, (a_c^+ + a_c) \tag{5.2.7b}$$

simulates the dynamics in $\mathbb{H}$

5.2b. Extensions to multimode systems.

We now turn to the multimode problem. The most general hamiltonian in this case is

$$H = \sum_i |e_i\rangle \epsilon_i \langle e_i| + \omega_c\, a_c^+ a_c + \sum_{i \neq j} |e_i\rangle [\, V_c \, (a_c^+ + a_c)] \langle e_j|$$

$$+ \sum_t \omega_t\, a_t^+ a_t + \sum_{t,i} |e_i\rangle (V_t^{(i)} [a_t^+ + a_t]) \langle e_i| . \tag{5.2.8}$$

Note that, the coupling modes cannot tune the electronic state energy and the tuning modes cannot cause coupling between the states due to symmetry constraints. Defining the auxiliary parameters

$$V_t = 0.5 (V_t^{(1)} + V_t^{(2)}) \tag{5.2.9a}$$

$$U_t = 0.5 (V_t^{(1)} - V_t^{(2)}) \tag{5.2.9b}$$

it can be shown that the mode 1 hamiltonian

$$\bar{H}_1 = \sum_{n=t,c} \omega_n a_n^+ a_n + \sum_t V_t (a_t^+ + a_t) - \epsilon \cos(\pi \sum_c a_c^+ a_c)$$

$$- \sum_t U_t (a_t^+ + a_t) \cos (\pi \sum_c a_c^+ a_c) + V_c (a_c^+ + a_c) \tag{5.2.10}$$

simulates the dynamics of H in $\mathbb{H}$ in $\mathbb{H}$ Change of sign in front of ϵ and U. generates $\bar{H}_2$ which simulates the dynamics in $\mathbb{H}_2$. Equation (5.2.10) defines the desired single surface hamiltonian that mimics the dynamics of the multisurface hamiltonian (5.2.8).

5.2c. Quadratic Lie-algebraic Approach.

We now use the coherent state operator algebra to calculate the dynamics of this system [1,2]. In this method, we parametrize the evolution operator as a product of exponentials generated by the elements of the n-dimensional harmonic oscillator algebra

$$L_n = \{ 1, a_i^+ , a_i , a_i^+ a_j^+ , a_i a_j , a_i^+ a_j \}, \tag{5.2.11}$$

Since we are particularly interested in the dynamics of the vacuum state, it is convenient to parametrize the evolution operator as

$$U = \exp\Big[\sum_i S_1^i a_i^+ + \sum_{i\le j} S_2^{ij} a_i^+ a_j^+\Big] \exp\Big[-\sum_i T_1^i a_i - \sum_{i\le j} T_2^{ij} a_i a_j\Big]$$

$$X \exp[S_0]. \qquad (5.2.12)$$

The expression for the autocorrelation turns out to be very simple as discussed in chapters 2 and 3. For computational simplicity, we have included only diagonal terms in S and T and dropped the shift operators a^+a from the ansatz (5.2.12). This amounts to the Hartree approximation [26]. Substituting the above ansatz in the TDSE, we obtain the following equations of motion for the case of one coupling and n tuning modes. The equations of motion for the case of only the coupling mode are obtained by putting $V = U. = \omega = 0$. The term $U \cos(\pi a^+a) U$ which results from the multicommutator expansion of $U HU$ is rearranged as $\exp(Xa_c)\cos(\pi a_c a_c)\exp(Ya_c)$ where X and Y are constants. The detailed derivation is given in Appendix 5.2.

$$i\dot{S}_2^c = 2\omega_c S_2^c - 2c(\varepsilon-u) S_1^{c2} \qquad (5.2.13a)$$

$$i\dot{S}_1^c = 4c(\varepsilon-u) S_1^{c2} T_1^c + \omega_c S_1^c + V_c + 2V_c S_2^c + 2(\varepsilon-u) c S_1^c \qquad (5.2.13b)$$

$$i\dot{T}_2^c = -2\omega_c T_2^c + 2c(\varepsilon-u)(S_1^{c2} - 4 S_1^c T_2^c T_1^c) \qquad (5.2.13c)$$

$$i\dot{T}_1^c = -\omega_c T_1^c - V_c + 2cT_1^c(-\varepsilon+u) - 8c(-\varepsilon+u) S_1^c T_2^c \qquad (5.2.13d)$$

$$i\,\dot{S}_2^t = 2\omega_t\,S_2^t \tag{5.2.13e}$$

$$i\,\dot{S}_1^t = \omega_t S_1^t + V_t + 2V_t\,S_2^t + cU_t\,(1+2S_2^t) \tag{5.2.13f}$$

$$i\,\dot{T}_2^t = -2\omega_t\,T_2^t \tag{5.2.13g}$$

$$i\,\dot{T}_1^t = -\omega_t\,T_1^t - V_t - c\,U_t \tag{5.2.13h}$$

$$i\,\dot{S}_0 = V_c\,S_1^c + V_t\,S_1^t + (-\varepsilon+u)\,c\,[2S_1^{c2}\,T_1^{c2} - 4S_1^{c2}\,T_2^c + 2S_1^c\,T_1^c]$$

$$+\,c\,[-\varepsilon + U_t\,S_1^t] \tag{5.2.13i}$$

where,

$$c = \exp\,[4T_2^c\;S_1^{c2}]\,\exp\,[-2\,T_1^c\,S_1^c] \tag{5.2.14a}$$

and

$$u = \sum_t U_t\,(S_1^t + T_1^t + 2S_2^t\,T_1^t) \tag{5.2.14b}$$

Here the subscripts c and t refer to the coupling and the tuning modes respectively. The values of the constants for the systems we have studied are given in Table 5.2.1.

5.2d. Results and Discussion.

We have applied the formalism to evaluate the Franck-Condon spectra of some model one dimensional systems containing only a coupling mode. As the tuning modes which modulate the electronic

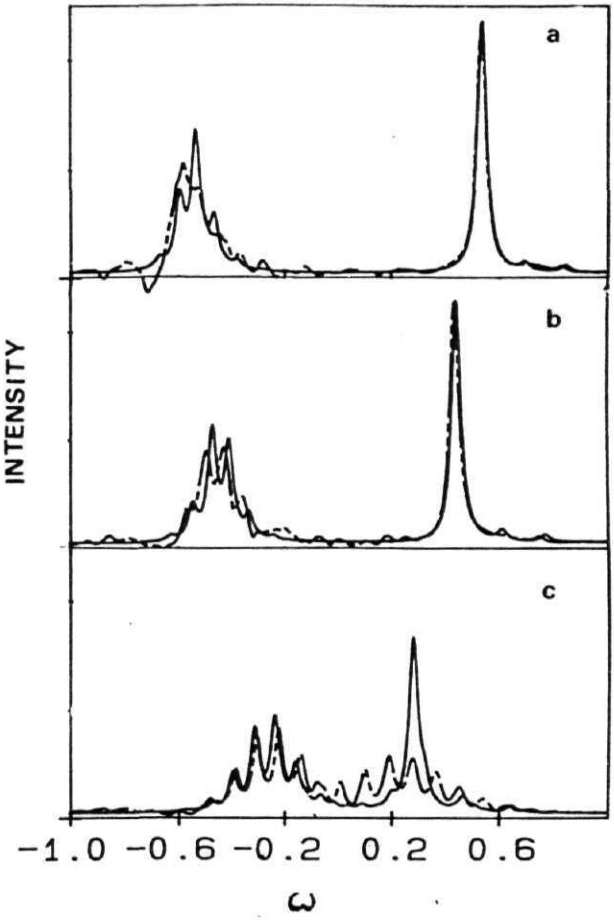


Fig. 5.2.1: Franck-Condon spectra of model one dimensional systems for different values of ε at $V_c = 0.318$ and $\omega_c = 0.091$: a) $\varepsilon = 0.5$, b) $\varepsilon = 0.4$ and c) $\varepsilon = 0.2$. All the values are in electron volts. The solid line indicates the exact spectrum and the dashed line indicates the spectrum obtained from algebraic calculations.

energy gap in the system are absent, the dependence of the electronic energy gap and the coupling constant on the spectra have been studied. We have also obtained the Franck-Condon spectra of a few **multidimensional** realistic systems. The absorption spectrum is obtained by fourier **transforming** the **autocorrelation** function A(t) which is given by

$$A(t) = \langle 0 | \; U \; | 0 \rangle \qquad (5.2.15a)$$

$$= \exp \; (S_0) \qquad (5.2.15b)$$

We first discuss the application to model single mode systems. The spectra for ε - 0.2, 0.4, 0.5 eV and V_c = 0.318 eV are shown in **Fig**. 5.2.1a, b and c. For ε = 0.2, the spectrum corresponding to the lower surface has been reproduced fairly well compared to the exact one. In contrast, the upper surface is not well reproduced. Instead of a single peak as seen in the exact spectrum, the algebraic approach produces a harmonic like progression. As the energy gap ε is increased to 0.4 and 0.5 eV, the agreement between the algebraic approach and the exact spectrum increases. This implies that as the energy gap increases, the **validity** of algebraic approach improves. The reason for this behaviour can be explained as follows. Consider the case when c is equal to zero. The **adiabatic hamiltonians** associated with the **hamiltonian (eq.5.1.1)** on both surfaces are essentially that of a displaced harmonic oscillator. This property is retained for small ε values and hence a harmonic progression for the upper surface for ε = 0.2 eV is seen (the lower surface anyway shows a harmonic like progression). For large energy gaps i.e, ε - 0.4 and 0.5 eV this progression is not

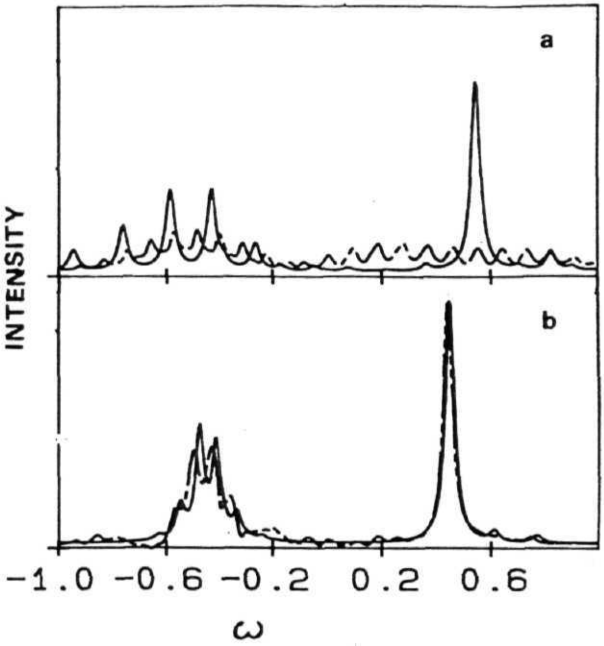


Fig. 5.2.2: Franck-Condon spectra of model one dimensional systems for different values of V_c at $\epsilon = 0.5$ and to$_c$ = 0.091: a) $V_c = 0.718$ and b) $V_c = 0.318$. All the values are in electron volts. Figure conventions are as in Fig.5.1.1.

seen since the deformation from the harmonic behaviour is more. In these cases the spectra by the algebraic approach are in good agreement with the exact spectra.

Increasing the coupling constant has the effect equivalent to decreasing the energy gap since the stabilization energy goes proportional to the square of the coupling constant. As can be seen in Fig. 5.2.2, the quality of the spectrum deteriorates when V = 0.718 eV even for c = 0.5 eV.

We have next calculated the photoelectron spectrum of a model system that is identical to butatriene cation in all aspects except that the energy gap at the origin is taken as 0.8 eV (double the value of butatriene), and allene which is an example where both the electronic surfaces under consideration are degenerate [61. Both are examples of two mode systems. These systems consist of one coupling mode and one tuning mode. Calculations have been also been performed by rearranging the term $[U^{-1}\cos(\pi a_c^{+} a_c)U]$ in $U^{-1} H U$ as $[e^{Xa_c^{+}} e^{Ya_c} \cos(\pi a_c^{+} a_c)]$ where X and Y are C-number functions of time. All the equations are identical except eq (5.2.13d) which is replaced by

$$i\dot{T}_1^{c} = -\omega_c T_1^{c} - V_c - 2cT_1^{c}(-\varepsilon+u). \qquad (5.2.16)$$

We call these set of equations aa the second **set** (eq.5.2.13d replaced by eq. 5.2.16) and the equations (5.2.13) as the first **set** in our discussion. Unless specifically mentioned, we imply that the spectra have been obtained from the first set of equations. In both the cases the equation for iT^{c}_{1} differs and the equations for the rest of the operators are identical. The spectra obtained in both the cases differ from each other as can

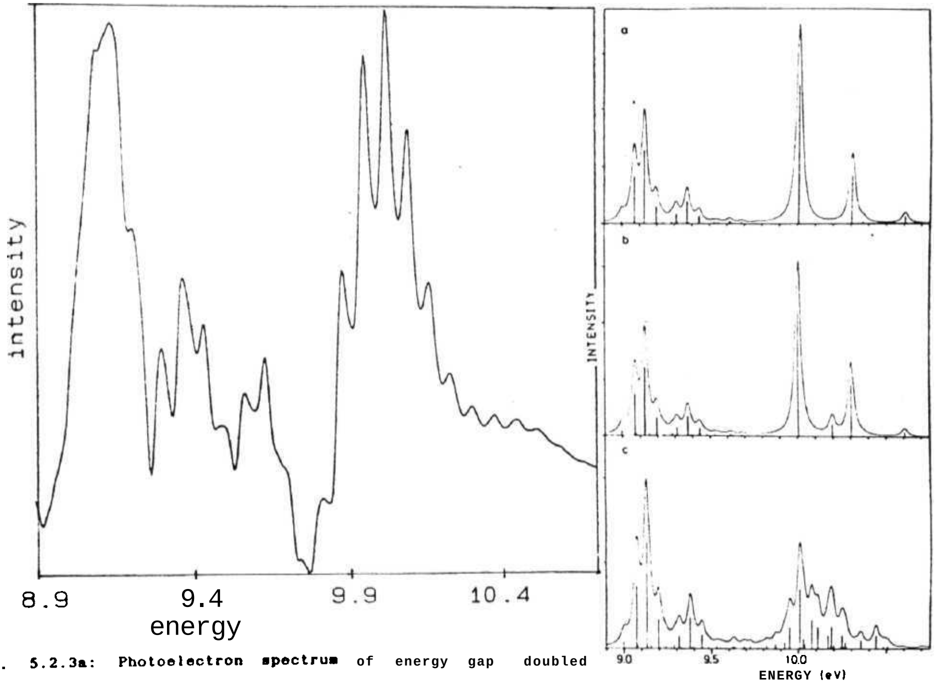


Fig. 5.2.3a: Photoelectron spectrum of energy gap doubled butatriene by the quadratic Lie-algebraic approach. The band at 0.15 eV is the mystery band obtained using the first set of equations. The inserts a, b and c are the Franck-Condon, adiabatic and theoretically exact spectra respectively (8).

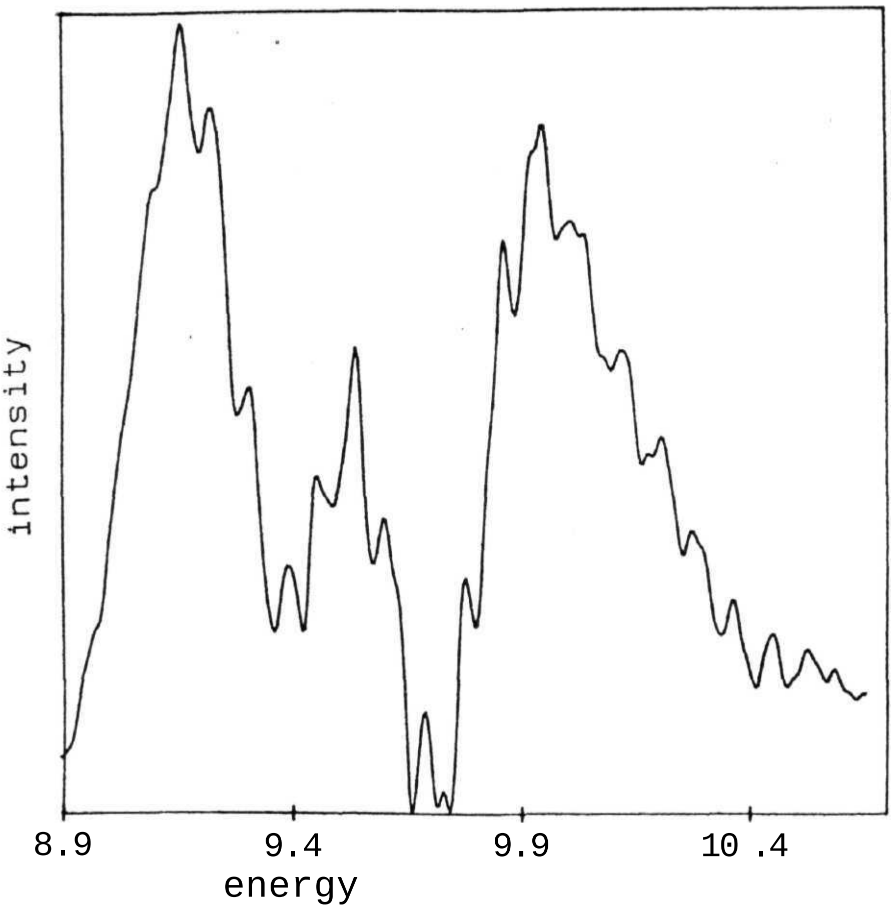


Fig. 5.2.3b: Photoelectron spectrum of energy gap doubled butatriene by the quadratic Lie-algebraic approach. The band at 9.5 eV is the mystery band obtained using the second set of equations.

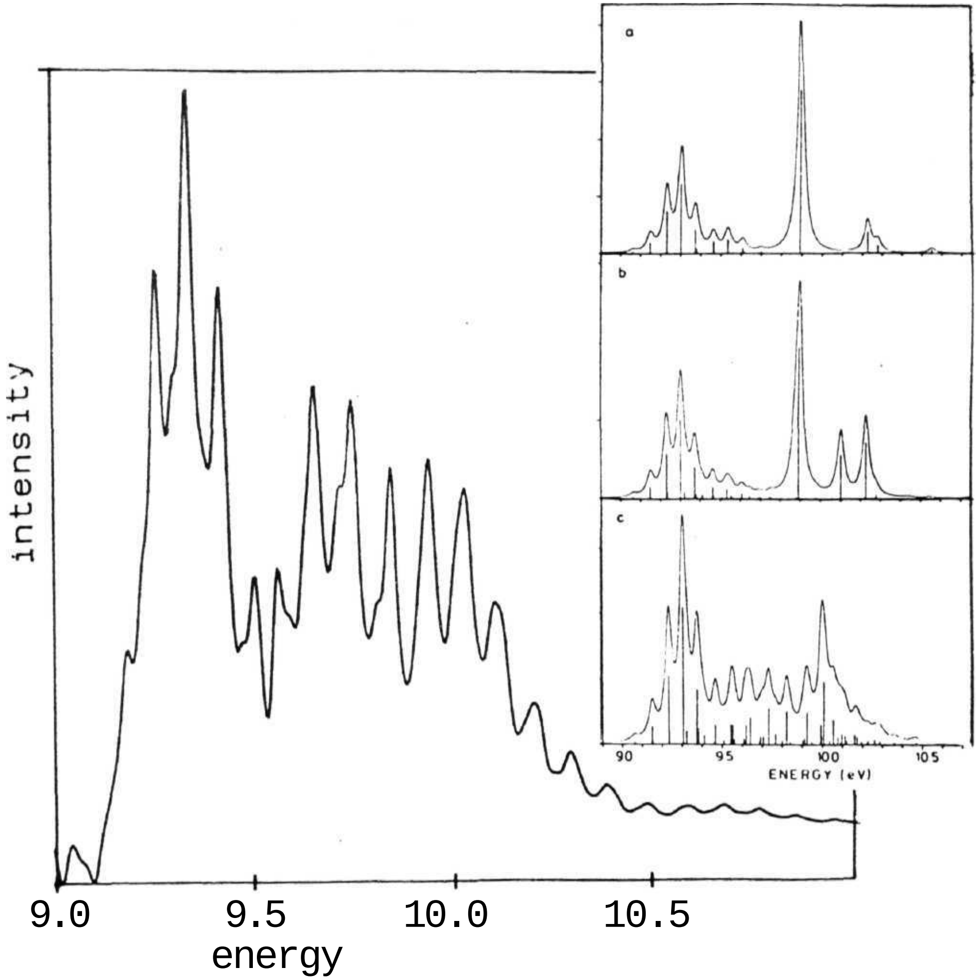


Fig. 5.2.3c: Photoelectron spectrum of butatriene by the quadratic Lie-algebraic approach. The inserts a,b and c are the Franck-Condon, adiabatic and theoretically exact spectra respectively [6].

be seen from Fig. 5.2.3a and 5.2.3b. This implies that the spectra depend on the manner in which the operators are arranged in the effective hamiltonian. An interesting feature of the energy gap doubled butatriene system and the original butatriene (Fig. 5.2.3c) system is that the spectrum shows three distinct bands while there are only two electronic states. The middle band in the PES of butatriene was named the mystery band by Brogli *et at* [301 for this reason. That this band appears due to vibronic coupling was shown by Cederbaum and co-workers [6]. As can be seen, the spectrum obtained from the algebraic approach is in good agreement except for a few minor shifts, with the exact spectrum and even the mystery band is generated in it. The spectra obtained from the algebraic approach is in better agreement with the exact than the corresponding Franck-Condon and adiabatic spectra shown in the inserts. Allene showed a better agreement with the exact spectrum than the Franck Condon spectrum (Fig. 5.2.4), but the density of states in the high energy part of the spectrum is less than that seen in the exact. Allene gave identical spectra with both sets of equations.

We further carried out calculations on pyrazine which is an example of a three mode system. Again both the sets of equations have been used to obtain the spectra. The equations of motion were rather stiff in the second case due to which they could not be integrated sufficiently long to obtain reasonable spectra. The lower surface shows descrete bands (Fig. 5.2.5a) as seen in the exact spectrum but the bands have not been sufficiently resolved though the sparse vibronic structure associated with the S state of rotationally and vibrationally cold aromatic molecules is well reproduced. The band corresponding to the upper surface is

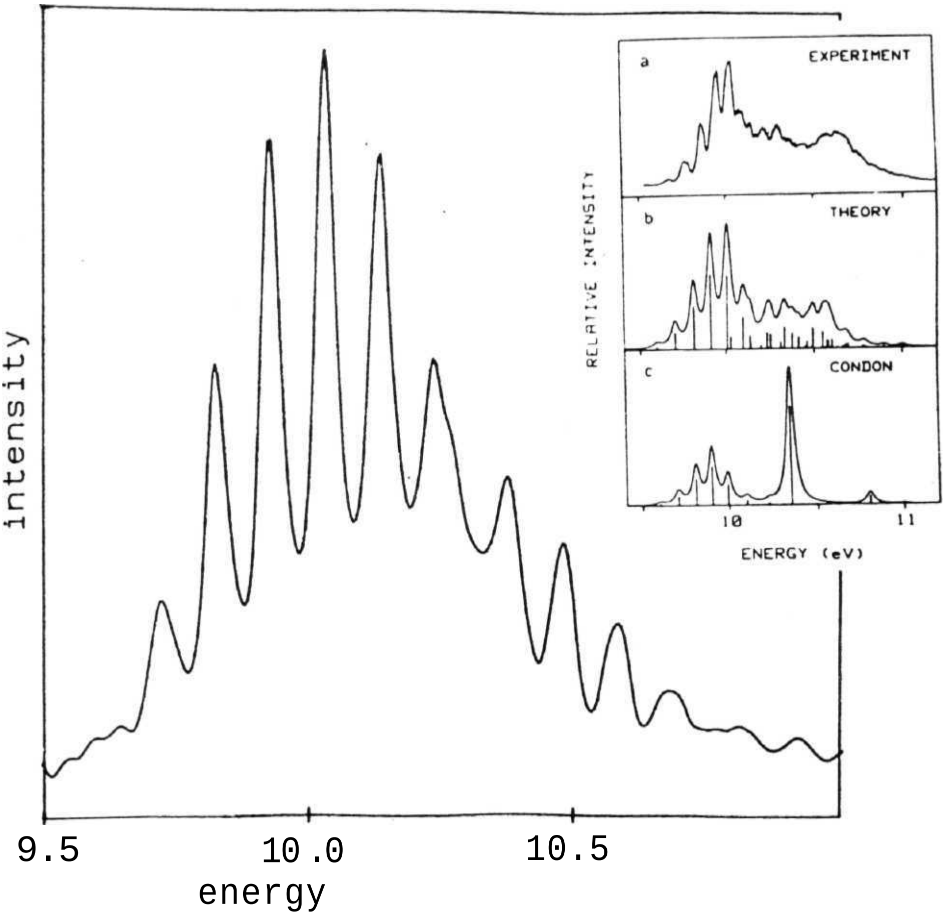


Fig. 5.2.4: Photoelectron spectrum of allene obtained from the quadratic Lie-algebraic approach. The inserts a,b and c are the experimental, theoretically exact and the Franck-Condon spectra respectively [6].

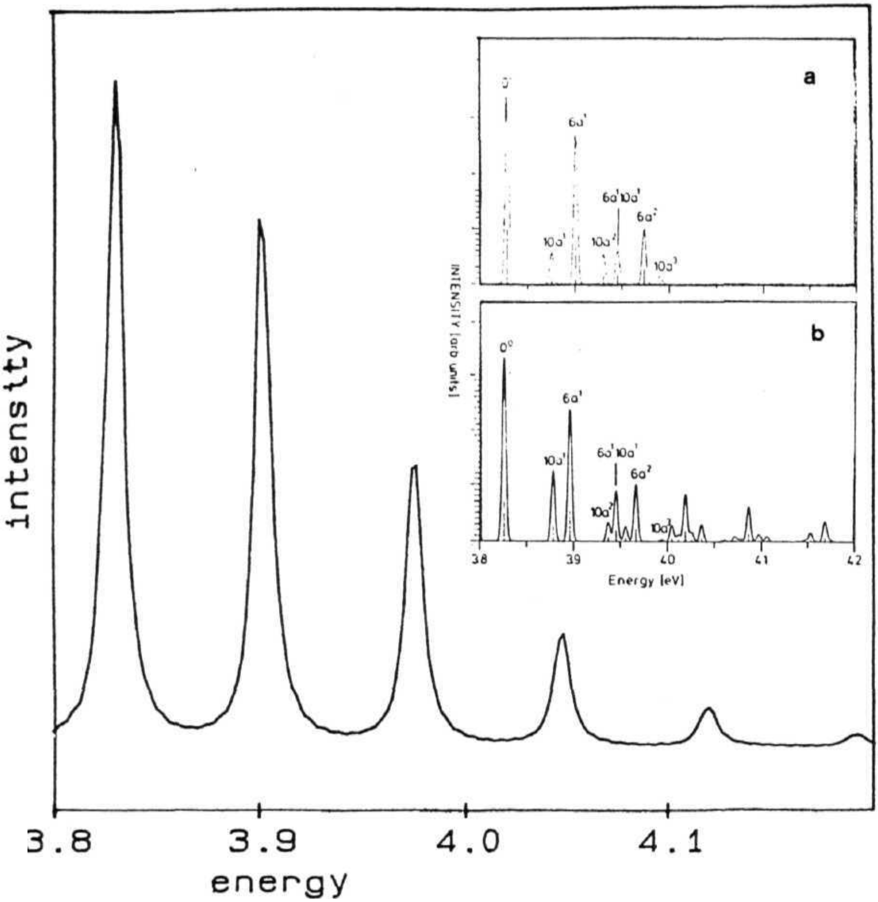


Fig. 5.2.5a: Photoelectron spectrum of the S_1 state of pyrazine by the quadratic Lie-algebraic approach. The inserts a and b correspond to the experimental and theoretical spectra respectively [13].

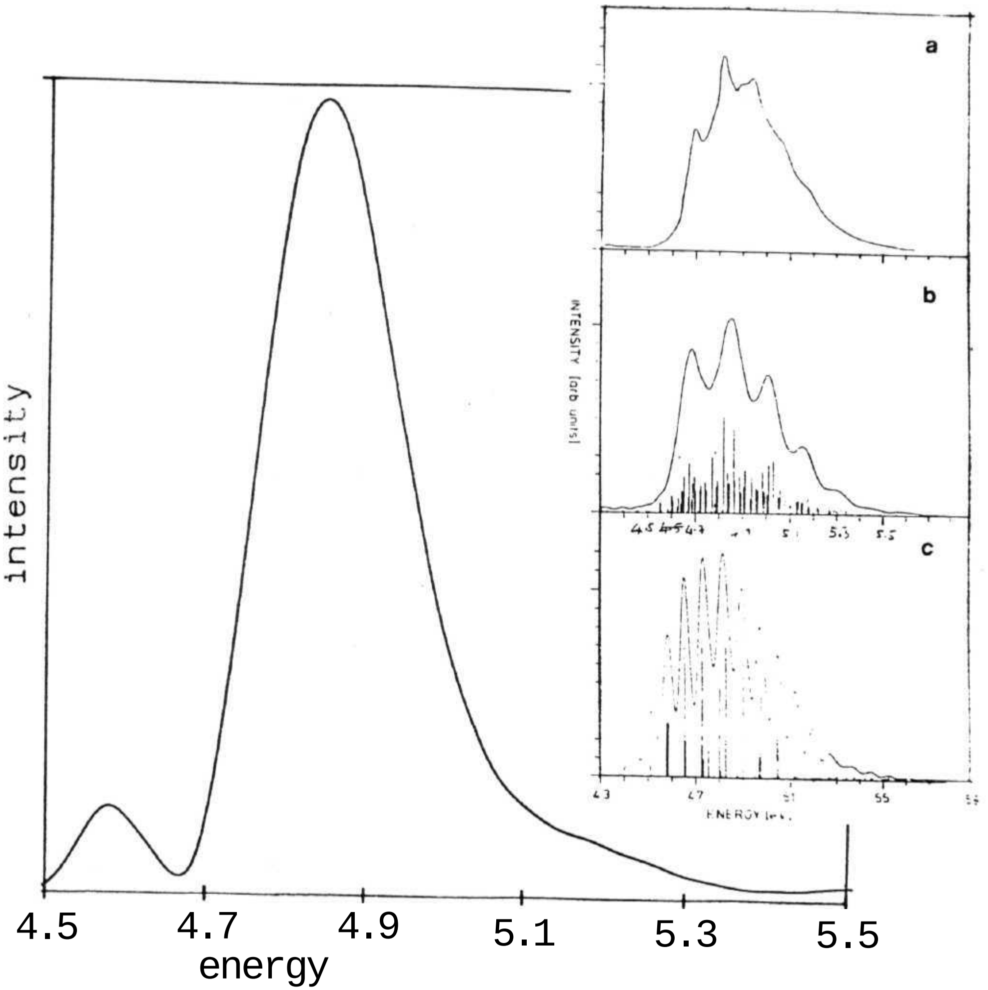


Fig. 5.2.5b: Photoelectron spectrum of the S_2 state of pyrazine by the quadratic Lie-algebraic approach. The inserts a,b and are the experimental, theoretical and the spectrum obtained in the absence of vibronic coupling respectively [13]

narrower than the exact spectrum Fig.(5.2.5b).

In all our calculations we required about thirteen equations to be integrated where as the basis set expansion methods to date require an order of 20 basis [10-20] in each degree of freedom to obtain the spectra. This computational simplicity is the main attraction of the algebraic theory.

TABLE 5.2.1

System		I [a]	II [b]
Butatriene	E [c]	9.450	9.850
	V_t/ω_g	-0.212/0.258	0.255/0.258
	V_c/ω_u	0.318/0.091	
Allene	E [c]	10.15	10.15
	V_t/ω_2	0.216/0.246	-0.216/0.246
	V_c/ω_1	0.339/0.107	
Pyrazine	E [d]	3.94	4.84
	V_t^1/ω	0.037/0.126	-0.254/0.074
	V_t^2/ω	-0.105/0.126	0.149/0.074
	λ/ω	0.262/0.118	

a Lower electronic surface.
b Upper electronic surface.
E Energy of the electronic surface.
V_t Force constants of the tuning modes.
ω Frequencies of the vibrational modes.
V_c Coupling constant.
c Ref. [6J.
d Ref. [13].

All the quantities are in eV

5.2e. Application of TDCCM to the non-adiabatic dynamics.

We next applied the TDCCM to obtain the dynamics of the system described by the hamiltonian in eq. (5.2.7a, b). Since we desire the evolution of the vacuum state only the time evolution operator U is given by

$$U = \exp[S] \tag{5.2.17a}$$

$$S = \Sigma s_m a^{+m}. \tag{5.2.17b}$$

Substituting the equation for U in the TDSE given by

$$iU^{-1} \dot{U} = U^{-1} H U \tag{5.2.18}$$

we obtain the working equations of motion given by

$$i \dot{S}_m = \Sigma m S_m \omega a^{+m} + \Sigma V_t m S a^{+m-1} + V_c a^{+}$$
$$+ \varepsilon \exp(-2 \sum_{m=\text{even}} S_m a^{+m}) \cos(\pi a^{+} a). \tag{5.2.19}$$

The equations obtained were very stiff and we could not integrate them for long enough times to obtain sufficiently resolved spectra.

S. 3. MULTIREFERENCE TDCCM(1) (MRTDCCM1): APPLICABILITY TO NON-ADIABATIC DYNAMICS.

As the TDCCM failed to describe the non-adiabatic dynamics of systems described by he hamiltonian eq.(5.1.1), we extend the formalism to include the complete algebra of the original unmapped hamiltonian. The advantage of MRTDCCM over single reference TDCCM discussed in section 5.2e is as follows. Let the ground state in the single reference TDCCM be ¦e > !0> where $|e_1\rangle$ and ¦0 > are the initial electronic and vibrational states respectively. As we consider only two electronic states in our applications to non-adiabatic dynamics the quadratic and the higher order electronic excitation operators generated by the exponential structure of the evolution operator give zero as only one electronic excitation is possible i.e, from the initial electronic state (!e.>) to the remaining state $(|e_2\rangle)$. In principle the attraction of TDCCM is that the higher order excitations are also taken into account by the virtue of the exponential ansatz for the evolution operator. The MRTDCCM on the other hand generates all the higher order electronic excitations as the multireference initial state is given by !e>!0> for i=1,2. Hence excitations from any one state leads to the other leading to the retainment of the higher order excitation operators. Therefore we expect the results to be better than the single reference TDCCM. This difference between the two methods holds good for any number of electronic states in which case many of the operators in the exponential ansatz do not contribute in the single reference TDCCM.

In this section, we discuss the application of MRTDCCM to the non adiabatic dynamics of systems described by the complete non-adiabatic unmapped hamiltonian in the linear coupling model. We show how the Lie-algebra to which the hamiltonian belongs can be decomposed to obtain decoupled equations of motion similar to the discussion in chapter 2.

5.3a. The Evolution Operator.

The general hamiltonian describing the nonadiabatic dynamics in the linear coupling model [6] is given by

$$H = \sum_i |e_i\rangle (E_i + H_i) \langle e_i| + V_c \tag{5.3.1}$$

where

$$H_i = \sum_n h_{in} \tag{5.3.2a}$$

$$h_{in} = \omega_n (a_n^+ a_n + 1/2) + V_n^{ii} (a_n^+ + a_n)/ \sqrt{2\omega_n} \tag{5.3.2b}$$

$$V_c = |e_1\rangle (V_c^{ij} / \sqrt{2\omega_n}) (a_n^+ + a_n) \langle e_2| \tag{5.3.2c}$$

where ω are the frequencies of the nth vibrational mode, V and V_c^{ij} are the intrastate and interstate coupling constants respectively.

We now analyse the Hibert space $\mathbb{H}$ relevent to the dynamics of this system. Let $\mathbb{H}_e$, $\mathbb{H}_v$ correspond to the Hilbert spaces of the electronic subsystem $\mathbb{H}$ and the vibrational subsystems $\mathbb{H}$ respectively. Then,

$$\mathbb{H} = \mathbb{H}_e \otimes \mathbb{H}_v \tag{5.3.3}$$

where

$$\mathbb{H}_e = \{ |e_j\rangle \}. \tag{5.3.4a}$$

The operator set corresponding to this Hilbert space is A_0

$$A_0 = \{ |i\rangle\langle j| \}$$

and

$$\mathbb{H}_v = \{ |n\rangle \}. \tag{5.3.4b}$$

The operator set corresponding to this Hilbert space is A .

$$A_n = \prod_\alpha a_\alpha^{m_\alpha} a_\alpha^{m_\alpha} . \tag{5.3.5}$$

We do not consider the direct product representation between the Hilbert spaces corresponding to the vibrational sub-spaces as the hamiltonian does not contain such terms. $\mathbb{H}$ now consists of the elements

$$\mathbb{H} = |e_i\rangle |n\rangle \cdot \tag{5.3.6}$$

The operator space corresponding IH to which the hamiltonian of the system belongs has the following elements,

$$L = \{ |i\rangle\langle k| \prod_\alpha a_\alpha^{m_\alpha} a_\alpha^{m_\alpha} \} \quad \forall\ i,k \text{ and } 0 \le m_\alpha,\ n_\alpha \le \infty \tag{5.3.7}$$

These elements form a Lie-algebra. We now show the construction of the time evolution operator which is essential to obtain the dynamics of the system. The Lie-algebra to which the hamiltonian belongs can now be decomposed in the following way.

$$C_0 = \{ |k\rangle \langle i| \prod_{\alpha} a_{\alpha}^{+\, n_{\alpha}} \; ; \; k, i=1,2 \text{ and } 1 \le n_{\alpha} \le \infty \}. \qquad (5.3.8)$$

$$D_0 = |k\rangle \langle i| \qquad (5.3.9)$$

$$L_1^{'} = \{ |k\rangle \langle i| \prod_{\beta,\alpha=1}^{D} a_{\alpha}^{+\, n_{\alpha}} \, a_{\beta}^{n_{\beta}} ; \; k, \; i=1,2 \; ; \; 0 \le n_{\alpha} \le \infty \text{ and } \sum_{\beta} n_{\beta} > 0 \}. \qquad (5.3.10)$$

With this, U can be parametrized similar to the time dependent generalisation of the NCCM ansatz discussed in chapter 2.

$$U = U_0 \, U_1 \ldots\ldots \qquad (5.3.11a)$$

$$U_0 = \exp \Big[\sum_{i,k} |i\rangle \langle k| \sum_{n_1 n_2 \ldots} S^{ik}_{n_1 n_2 \ldots} (a_1^{+})^{n_1} (a_2^{+})^{n_2} \ldots + S^{0}_{00} \Big] \qquad (5.3.11b)$$

$$U_1 = \exp \Big[\sum_{i,k} |i\rangle \langle k| \sum_{\alpha} \sum_{n_1 n_2 \ldots} S^{ik}_{n_1 n_2 \ldots ; \alpha} (a_1^{+})^{n_1} (a_2^{+})^{n_2} \ldots a_{\alpha} \Big]. \qquad (5.3.11C)$$

We now study the ground state propagation of the system and obtain the autocorrelation function to obtain the spectra. The time evolution operator corresponding to the ground state propagation is given by

$$U |0\rangle = U_0 |0\rangle \qquad (5.3.12a)$$

$$U_0 = \exp \Big[\sum_{i,k} |i\rangle \langle k| \sum_{n_1 n_2 \ldots} S^{ik}_{n_1 n_2 \ldots} (a_1^{+})^{n_1} (a_2^{+})^{n_2} \ldots + S^{0}_{00} \Big]. \qquad (5.3.12b)$$

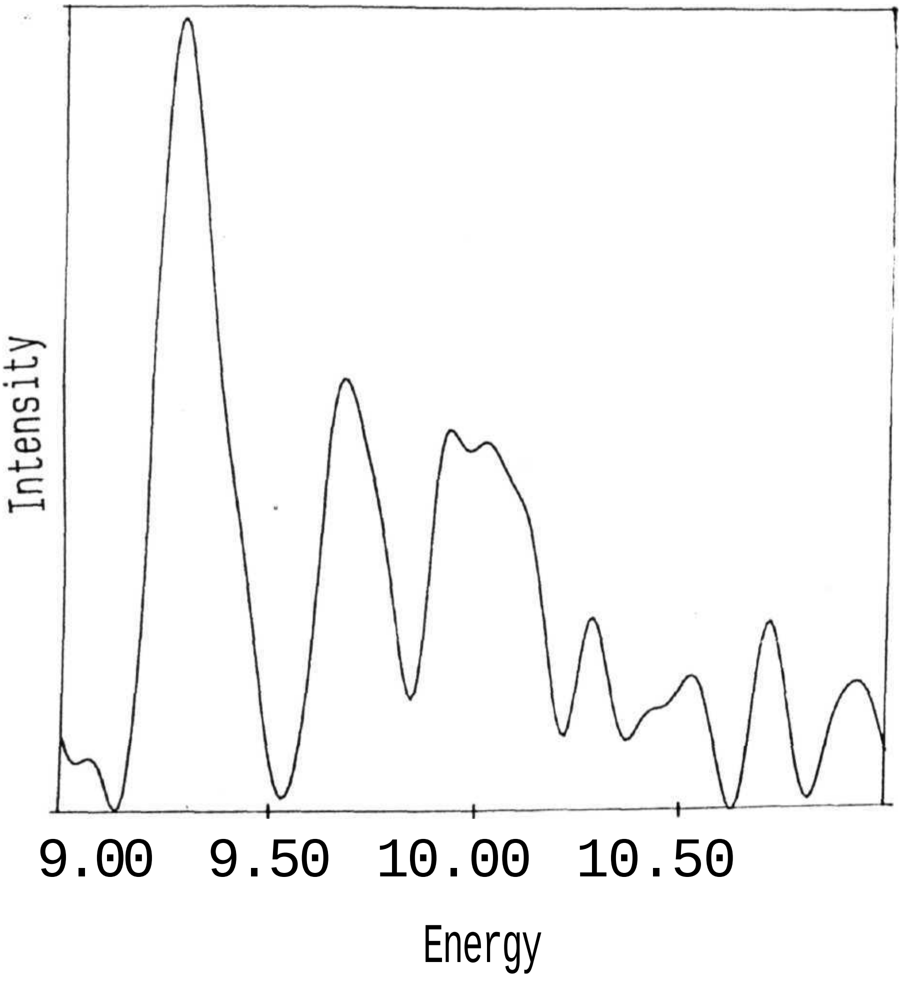


Fig. 5.3.1b: Photoelectron spectrum of butatriene obtained from MRTDCCM1.

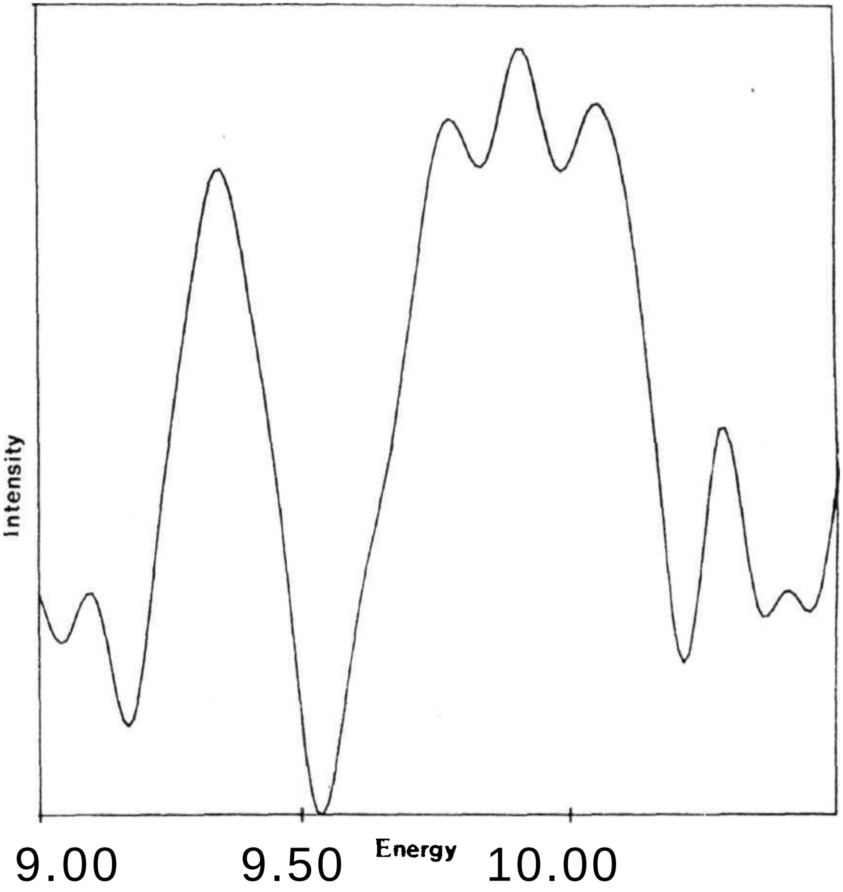


Fig. 5.3.1a: **Photoelectron spectrum** of the upper surface of butatriene obtained from **MRTDCCM1**.

The equations of motion are obtained by solving the TDSE which we do so by the conventional diagrammatic approach [31]. The diagrams obtained in this case are shown in appendix 5.3.

5.3b. Numerical studies.

We have applied the above formalism to obtain the spectra of a few realistic systems. In all the cases, we have truncated the cluster operator such that no more than one boson operator was included due to lack of computational resources, no convergence studies were undertaken. The spectrum of butatriene upper surface is presented in Fig. 5.3.1a. The lower surface could not be integrated for sufficiently long to obtain a reasonably resolved spectrum at this level of approximation. The total spectrum of butatriene is presented in Fig. 5.3.1b. The spectrum is not in good agreement with the exact as the integration of the equations of motion could not be performed for sufficiently long. In spite of this, the three bands seen in the exact butatriene spectrum are seen in this cace also.

We next present the S_2 surface of pyrazine in Fig. 5.3.2. Good agreement with the exact spectrum is seen. In this system the density of states is so high that only a homogenously broadened envelope is seen which does not require integration for long times to obtain a reasonably good spectrum. The spectrum for allene could not be obtained as the equations were too **stiff** to be integrated for long times.

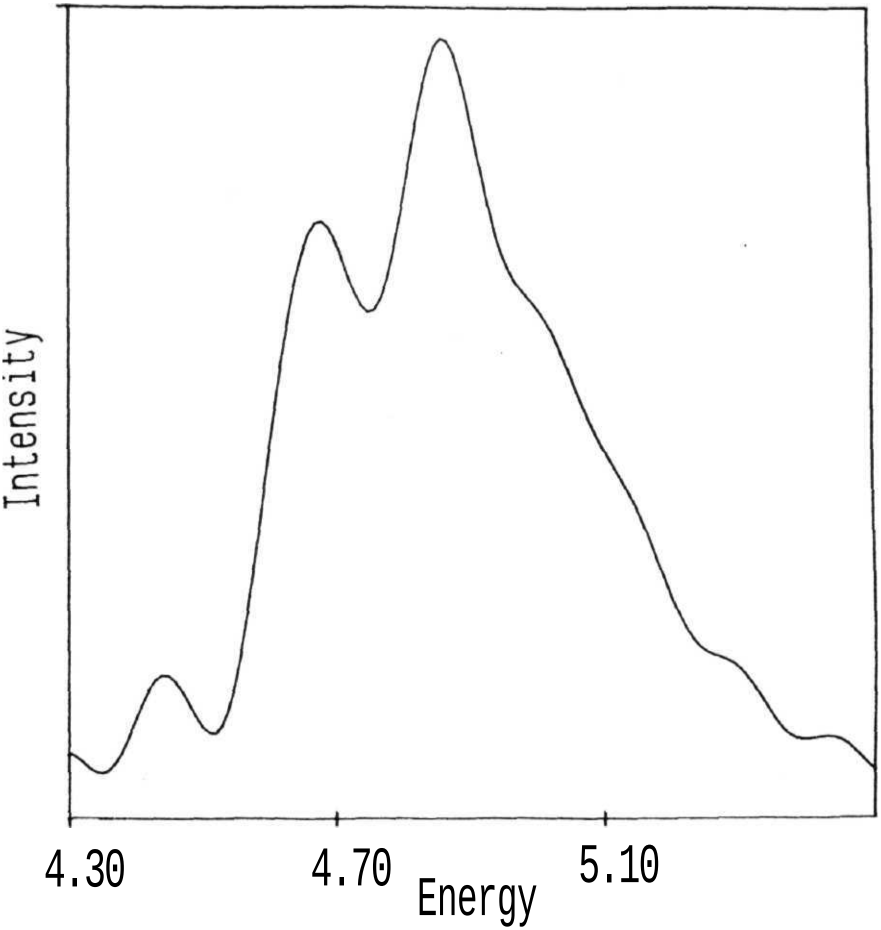


Fig. 5.3.2:. Photoelectron spectrum of the S_2 state of pyrazine obtained from MRTDCCM1.

5.4.. **MRTDCCM2.**

As we could not integrate the equations of motion for sufficiently long by applying the methodology discussed in Sec. 5.3, we tried an alternative procedure which we discuss in this section.

5.4a. The evolution operator.

The hamiltonian is as given by eq.(5.3.1) and (5.3.2). In these equations, the electronic degrees of freedom and the coupling mode interact strongly. Keeping this in mind we combine them together and rewrite the hamiltonian as

$$H = \sum |i> E_{ij} <j| + \sum_{t} \omega_t (a_t^+ a_t + 1/2) + \sum_{i,t} |i> V_n^{ii} (a_t^+ + a_t)/\sqrt{2\omega}_t <i| \tag{5.4.1}$$

where,

$$E_{ij} = |i> [\, E_i \delta_{ij} + \omega_c (a_c^+ a_c + 1/2) + (1 - \delta_{ij}) (V_c^{ij} / \sqrt{2\omega}_c) (a_c^+ + a_c)] <j| \tag{5.4.2}$$

where the subscripts t and c denote the tuning and coupling modes **respectively.** $|j><k|$ represent the projection operators in the **Hilbert** space of the combined electronic **subsystem** and **a** and a. are the boson **annilhilation** and creation operators of the ith vibrational mode.

We now analyse the Hilbert space $\mathcal{H}$ relevent to the dynamics of this system. Let $\mathcal{H}_{ec}$, $\mathcal{H}_{v}$ correspond to the Hilbert spaces of the combined electronic and coupling mode subsystems $\mathbb{H}_{ec}$ and the tuning mode subsystem $\mathbb{H}$ respectively. Then,

$$\mathbb{H} = \mathbb{H}_{ec} \otimes \mathbb{H}_{v} \tag{5.4.3}$$

where

$$\mathbb{H}_{ec} = \{ |e_j\rangle |n_c\rangle \}. \tag{5.4.4a}$$

The operator set corresponding to this Hilbert space is A_0.

$$A_0 = \{ |i\rangle\langle j| \} \tag{5.4.4b}$$

$$\mathbb{H}_{v} = \{ |n\rangle \}. \tag{5.4.5a}$$

The operator set corresponding to this Hilbert space is given by

$$A_\alpha = \{ \prod_\alpha a_\alpha^{m_\alpha} a_\alpha^{m_\alpha} \} \tag{5.4.5b}$$

where α corresponds to the tuning mode subsystem. The Lie algebra corresponding to this hamiltonian is identical in structure to eq.(5.3.7) except that $|i\rangle\langle k|$ now correspond to the combined electronic and vibrational subsystems. The same is the case for the evolution operator given by equations 5.3.11 and 5.3.12. The diagrams are identical to those obtained in the previous section.

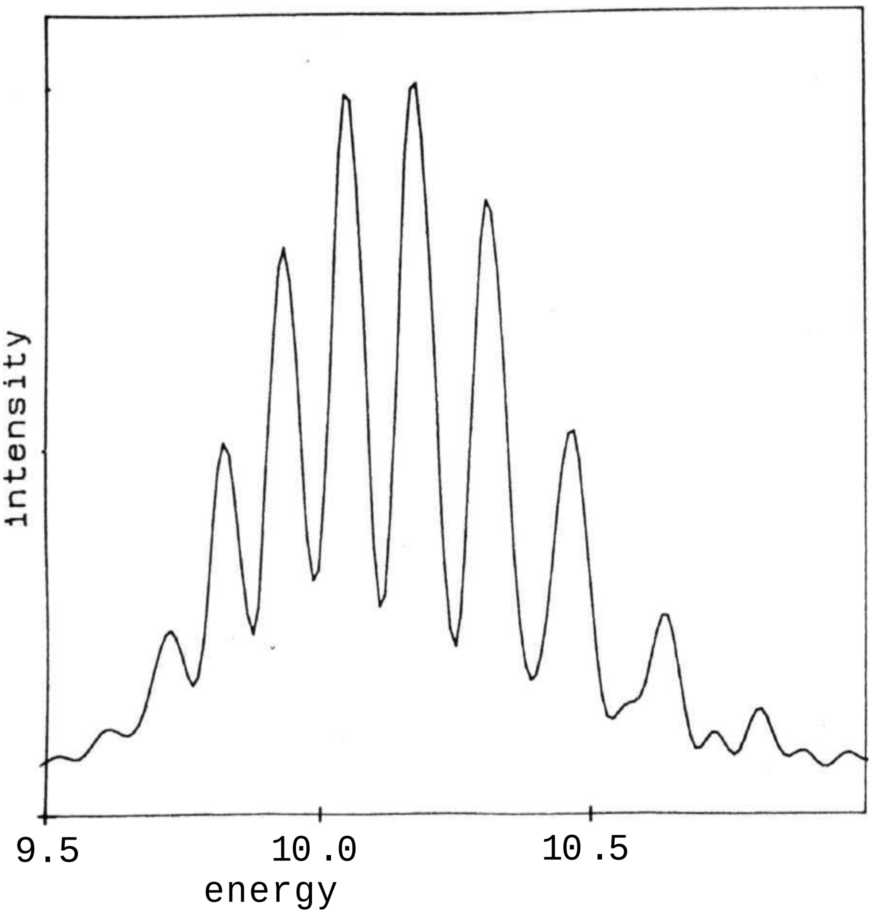


Fig. 5.4.1: Photoelectron spectrum of allene obtained froa MRTDCCM2.

5.4b. Numerical Studies.

We have applied the formalism discussed in Sec.5.4a again in the one boson approximation to obtain the photoelectron spectra of allene (Fig. 5.4.1), and butatriene (Fig. 5.4.2a corresponding to the upper surface and Fig. 5.4.2b corresponding to the total spectrum). The spectrum for allene does not show the large density of states seen in the latter part of the exact spectrum. This result is similar to that obtained in the case of the surface mapped hamiltonian discussed in Sec. 5.2 using the quadratic Lie-algebraic approach. The first part of the spectrum obtained for butatriene is in good agreement with the exact spectrum although the intensity seen in the latter part of the spectrum is overestimated which we attribute to the fact that the lower surface could not be integrated for sufficiently long times. In this formalism the spectrum for pyrazine could not be obtained.

5.5. CONCLUSIONS.

In this work we have applied the coherent state algebraic formalism [1,21, which corresponds to the GWP [22-26] in the coordinate space, to calculate the dynamics of non-adiabatic systems, specifically consisting of two electronic states belonging to different symmetries. In GWP, the potential is expanded as a Taylor series around the centroid of the wavepacket. The difficulty in chosing the centroid of the wavepacket which comprises of two nuclear wave functions corresponding to the two electronic functions having two

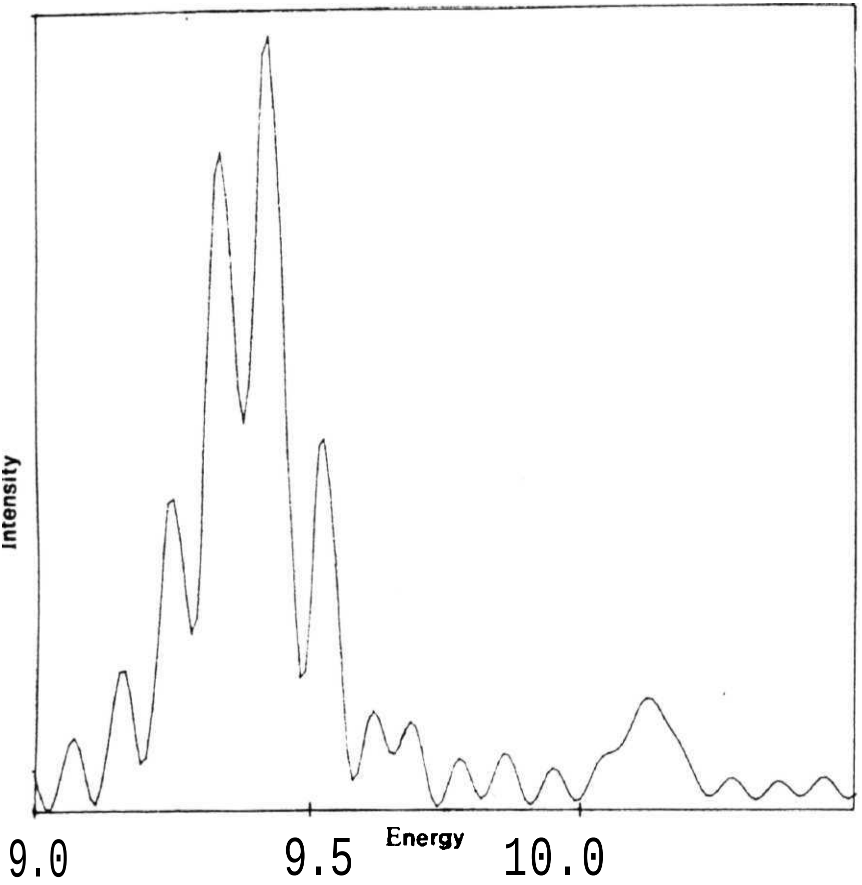


Fig. 5.4.2a: Photoelectron spectrum of the upper surface of butatnene **obtained from MRTDCCM2.**

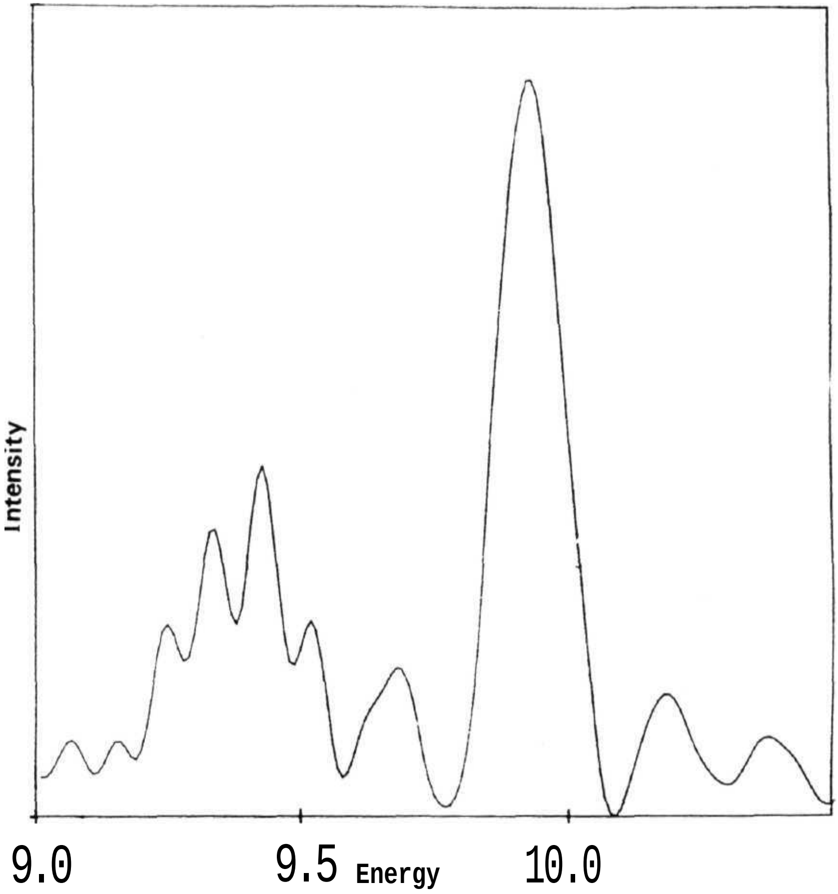


Fig. 5.4.2b: Photoeleotron apectrua of butatriene **obtained from MRTDCCM2.**

different centroids and momenta, has led us to construct a new hamiltonian which is explicitly independent of the involved electronic states. This has been done by mapping the original hamiltonian on to a hamiltonian associated with a single electronic surface.

Using the new hamiltonian we have calculated the spectra for a few model systems comprising of two electronic states and one vibrational (coupling) mode to study the sensitivity of the coupling constants and the energy gap between the two electronic states on the spectrum. It has been found that for the single vibrational mode (having no tuning modes which modulate the electronic energy gap) case the accuracy of the Lie-algebraic approach increases as the energy gap between the two surfaces increases. For a small ϵ, the spectrum associated with the lower surface is well reproduced, but the upper surface dynamics are quite inaccurate.

For the multimode case, two sets of ansatz have been used to obtain the spectra differing only in the equation for T_1^c corresponding to the single boson annihilation operator of the coupling mode. Except for energy gap doubled butatriene, the equations of motion obtained by using the second set of equations were too stiff to be integrated upto sufficiently long times to obtain the spectra. This shows that the calculated spectra are dependent on the manner in which the operators in the effective hamiltonian are chosen. The photoelectron spectra of allene, butatriene and pyrazine obtained from the first set of equations of motion given by eq.(5.2.14) gave a good overall spectra.

We have also tried to evaluate the spectra using the TDCCM approach, but the equations were found to be too stiff to be integrated for sufficiently long times to obtain spectra. We observed however that till the time period we could integrate, the TDCCM values of the autocorrelation function tallied very well with the exact values.

As the TDCCM failed to account for the dynamics of the system decribed by the mapped hamiltonian, we tested the applicability of the multireference TDCCM (MRTDCCM) to the unmapped hamiltonian involving explicitly the electronic degrees of freedom. Two different evolution operators were considered. In one the electronic and the coupling mode subsystems were combined as the interaction between them is strong and in the other the elctronic subsystem is decoupled from the vibrational subsystem totally. We found that the equations are quite stiff in both the cases, but were more flexible than the single reference TDCCM. In all the cases the short time dynamics is well reproduced at one boson approximation level. But the long time dynamics (even beyond 50 fs.) could not be obtained. Note that all the multimode systems studied here contain conical intersections close to the. Franck-Condon zone and consequently accessible to the wave packets started at the origin. As we found in Sec. 5.2, the wave packet approaches breakdown when the energy gap between the two surfaces is small. Thus, it is not surprising that the TDCCM approaches breakdown for these systems.

APPENDIX 5.2

We solve the TDSE to obtain the working equations of motion by the quadratic Lie-algebraic approach applied to the non-adiabatic dynamics corresponding to the surface mapped hamiltonian discussed in Sec. 5.2. The time evolution operator is given by

$$U = \exp\left[\sum_i S_1^i a_i^+ + \sum_{i \le j} S_2^i a_i^+ a_i^+ \right] \exp\left[-\sum_i T_1^i a_i + \sum_{i \le j} - T_2^i a_i a_i \right]$$
$$X \exp[S_0] \qquad (A5.1)$$

Substituting the above equation in the TDSE we obtain

$$iU^{-1} \dot{U} = U^{-1} H U \qquad (A5.2)$$

Considering the R.H.S. of the above equation we obtain by subbstituting eq.(5.2.10) for the hamiltonian

$$U^{-1} H U = U^{-1} \Big[\sum_{n=t,c} \omega_n a_n^+ a_n + \sum_{n=t,c} V_n (a_n^+ + a_n) - \epsilon \cos(\pi \sum_c a_c^+ a_c)$$
$$- \sum_t U_t (a_t^+ + a_t) \cos (\pi \sum_c a_c^+ a_c) \Big] U \qquad (A5.3)$$

where the superscript and the subscript n denotes commonly the tuning and the coupling modes. The subscripts c and t denote the coupling and the tuning modes respectively.

The first term in the above equation is obtained by applying the Hausdorff expansion [32].

$$
\begin{aligned}
U^{-1} [\omega_n a_n^+ a_n] U = {} & \omega_n a_n^+ a_n + \omega_n T_1^n a_n + 2 T_2^n \omega_n a_n a_n \\
& + S_1^n \omega_n a_n^+ + S_1^n T_1^n \omega_n + 2 S_1^n T_2^n \omega_n a_n + 2 S_2^n \omega_n a_n^+ a_n^+ \\
& + 4 S_2^n T_1^n \omega_n a_n^+ + 2 S_2^n T_2^{n2} \omega_n + 2 S_2^n T_2^n \omega_n (4 a_n^+ a_n + 2) \\
& + 8 S_2^n T_2^n T_2^n \omega_n a_n + 8 S_2^n T_2^n \omega_n a_n a_n
\end{aligned}
\qquad (A5.4)
$$

The second tern in eq. (A5.3) after the Hausdorff expansion is given by

$$
\begin{aligned}
U^{-1} [V_n (a_n^+ + a_n)] U = {} & V_n a_n^+ + T_1^n V_n + 2 T_2^n V_n a_n \\
& + V_n a_n + V_n S_1^n + 4 S_2^n T_2^n V_n a_n + 2 S_2^n V_n^n a_n^+ + 2 S_2^n T_1^n V_n
\end{aligned}
\qquad (A5.5)
$$

Considering the third term we obtain,

$$
\begin{aligned}
& U^{-1} [- \varepsilon \cos(\pi \sum_c a_c^+ a_c)] U = \\
& \exp [-S_0] \exp [T_1^c a_c] \exp [T_2^c a_c a_c] \exp [-S_1^c a_c^+] \exp [-S_2^c a_c^+ a_c^+] \\
& X [- \varepsilon \cos(\pi a_c^+ a_c)] \\
& \exp [S_2^c a_c^+ a_c^+] \exp [S_1^c a_c^+] \exp [-T_1^c a_c] \exp [-T_2^c a_c a_c] \\
& X \exp [S_0]
\end{aligned}
\qquad (A5.6)
$$

We now put the above equation in normal order i.e, all the annihilation operators are arranged to be to the extreme right so that the equations obtained for the vacuum state propagation simplify as these operators give zero acting on the vacuum state. By doing this rearrangement the equation for the auto correlation function also simplifies.

$\mathrm{Cos}(\pi\, a_c^+ a_c)$ can be written as $\exp(\, i\,\pi\, a_c^+\, a_c)$. Hence, the above equation can be rewritten as

$$\begin{aligned}
&= \exp[-S_0\,]\,\exp[\,T_1^c\,a_c\,]\,\exp[\,T_2^c\,a_c\,a_c\,]\,\exp[-S_1^c\,a_c^+] \\
&X\ \exp[-S_2^c\,a_c^+\,a_c^+\,]\ \exp(\,i\,\pi\,a_c^+\,a_c)\,\exp[\,S_2^c\,a_c^+\,a_c^+\,] \\
&X\ \exp[\,S_1^c\,a_c^+\,]\,\exp[-T_1^c\,a_c]\,\exp[-T_2^c\,a_c\,a_c\,]\ X\ \exp[S_0\,]
\end{aligned} \tag{A5.7}$$

$$\begin{aligned}
&= \exp[-S_0\,]\,\exp[\,T_1^c\,a_c]\,\exp[\,T_2^c\,a_c\,a_c]\,\exp[-S_1^c\,a_c^+]\,\exp[-S_2^c\,a_c^+\,a_c^+\,] \\
&X\ \underline{\exp(\,i\,\pi\,a_c^+\,a_c)\,\exp[\,S_2^c\,a_c^+\,a_c^+\,]\exp(-\,i\,\pi\,a_c^+\,a_c)}\,\exp(\,i\,\pi\,a_c^+\,a_c) \\
&X\ \exp[\,S_1^c\,a_c^+\,]\,\exp[-T_1^c\,a_c]\,\exp[-T_2^c\,a_c\,a_c\,]\ X\ \exp[S_0\,]
\end{aligned} \tag{A5.8}$$

The part of the equation **underlined** in the above equation can be expanded using the BCH expansion to obtain

$$\underline{\exp(\,i\,\pi\,a_c^+\,a_c)\,\exp[\,S_2^c\,a_c^+\,a_c^+\,]\exp(-\,i\,\pi\,a_c^+\,a_c)}$$

$$= \exp[\,S_2^c\,a_c^+\,a_c^+\,\exp(2\,i\pi)\,] \tag{A5.9}$$

$$= \exp[\,S_2^c\,a_c^+\,a_c^+\,] \tag{A5.10}$$

This follows from $\exp(2i\pi)$ being equal to 1. **Substituting** the above equation in **eq.** (A5.8) we obtain,

$$= \exp[-S_0] \exp[T_1^c a_c] \exp[T_2^c a_c a_c]$$

$$\times \exp[-S_1^c a_c^+] \exp(i \pi a_c^+ a_c) \exp[S_1^c a_c^+] \exp[-T_1^c a_c]$$

$$\times \exp[T_2^c a_c a_c] \exp[S_0] \qquad \textbf{(A5.11)}$$

Again the above equation can be rewritten similar to the previous manipulation as in eq. (A5.8) as

$$= \exp[-S_0] \exp[T_1^c a_c] \exp[T_2^c a_c a_c] \exp[-S_1^c a_c^+]$$

$$\times \underline{\exp(i \pi a_c^+ a_c) \exp[S_1^c a_c^+] \exp(-i \pi a_c^+ a_c)} \exp(i \pi a_c^+ a_c)$$

$$\times \exp[-T_1^c a_c] \exp[T_2^c a_c a_c] \exp[S_0] \qquad \text{(A5.12)}$$

The underlined part of the above equation is written as

$$\exp(i \pi a_c^+ a_c) \exp[S_1^c a_c^+] \exp(-i \pi a_c^+ a_c) =$$

$$\times \exp[S_1^c a_c^+ \exp(i\pi)] = \exp[-S_1^c a_c^+] \qquad \textbf{(A5.13)}$$

Substituting back in eq. (A5.12) we obtain

$$= \exp[-S_0] \exp[T_1^c a_c] \exp[T_2^c a_c a_c] \exp[-2S_1^c a_c^+]$$

$$\times \exp(i \pi a_c^+ a_c) \exp[-T_1^c a_c] \exp[T_2^c a_c a_c] \exp[S_0]$$

$$= \exp[-S_0] \exp[T_1^c a_c] \underline{\exp[T_2^c a_c a_c] \exp[-2S_1^c a_c^+]}$$

$$\underline{\exp[-T_2^c a_c a_c]} \exp[T_2^c a_c a_c]$$

$$\times \exp(i \pi a_c^+ a_c) \exp[-T_1^c a_c] \exp[T_2^c a_c a_c] \exp[S_0]$$

$$= \exp[-S_0]\exp[T_1^c a_c]\exp[-2S_1^c a_c^+ - 4S_1^c T_2^c a_c]$$

$$\times \exp[T_2^c a_c a_c]\exp(i\pi a_c^+ a_c)\exp[-T_1^c a_c]\exp[T_2^c a_c a_c]$$

$$\times \exp[S_0] \qquad (A5.14)$$

Using the relation

$$\exp[Z_1 a^+ + Z_2 a] = \exp[Z_1 a^+]\exp[Z_2 a]\exp[Z_1 Z_2] \qquad (A5.15)$$

$$\exp[-2S_1^c a_c - 4S_1^c T_2^c a_c] = \exp[-2S_1^c a_c^+]\exp[-4S_1^c T_2^c a_c]$$

$$\times \exp[4S_1^{c2} T_2^c] \qquad (A5.16)$$

Substituting this in eq. (A5.14) we obtain

$$= \exp[-S_0]\exp[T_1^c a_c]\exp[-2S_1^c a_c^+ \exp[-4S_1^c T_2^c a_c]$$

$$\times \exp[4S_1^{c2} T_2^c]\exp[T_2^c a_c a_c]\exp(i\pi a_c^+ a_c)\exp[-T_1^c a_c]$$

$$\times \exp[T_2^c a_c a_c]\exp[S_0] \qquad (A5.17)$$

Continuing in the same vein we finally obtain for the third term in eq. (A5.3)

$$U^{-1}[-\varepsilon\cos(\pi\sum_c a_c^+ a_c)]U =$$

$$c\exp[-2S_1^c a_c^+]\exp[i\pi a_c^+ a_c]\exp[-2S_1^c(1+2T_2^c)a_c]$$

$$(A5.18)$$

Similarly the last term in eq. (A5.3) can be evaluated to give

$$U^{-1}\left[-\sum_t U_t(a_t^+ + a_t)\cos\left(\pi \sum_c a_c^+ a_c\right)\right]U =$$
$$\underbrace{U^{-1}\left[-\sum_t U_t(a_t^+ + a_t)\right]U}\quad \underbrace{U^{-1}\left[\cos\left(\pi \sum_c a_c^+ a_c\right)\right]U} \qquad \text{(A5.19)}$$

The above equation is a product of two **Hausdorff** expansions shown by underlining both the parts. The evaluation of the two parts is similar to the way in which the second term and the third term of eq. (A5.3) have been evaluated. The resultant equation is

$$U^{-1}\left[-\sum_t U_t(a_t^+ + a_t)\cos\left(\pi \sum_c a_c^+ a_c\right)\right]U =$$
$$[\, U_n\, a_n^+ + T_1^n\, U_n + 2\, T_2^n\, U_n\, a_n + U_n\, a_n + U_n\, S_1^n + 4\, S_2^n\, T_2^n\, U_n\, a_n$$
$$+ 2\, S_2^n\, U_n^n\, a_n^+ + 2\, S_2^n\, T_1^n\, U_n\,]\; c\; \exp[-2\, S_1^c\, a_c^+\,]\; \exp[\,i\pi\, a_c^+ a_c]$$
$$X\; \exp[-2S_1^c(\,1 + 2T_2^c\,)a_c\,] \qquad \text{(A5.20)}$$

Combining equations (A5.4), (A5.5), (A5.18) and (A5.20) we obtain the equation for the R.H.S. of the TDSE. The L.H.S. is obtained similarly as

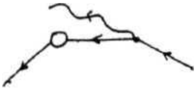
$$i\;U^{-1}\; d/dt\; U = \dot{S}_2 a_n^+ a_n^+ + 2\dot{S}_2 T_1 a_n^+ + \dot{S}_2 T_1^2 + \dot{S}_2 T_2\;(4a_n^+ a_n + 2)$$
$$+ 4\dot{S}_2 T_2 T_1 a_n + 4\dot{S}_2 T_2 a_n a_n + \dot{S}_1 a_n^+ + \dot{S}_1 T_1 + 2\dot{S}_1 T_2 a_n +$$
$$- \dot{T}_2 a_n a_n - \dot{T}_1 a_n + \dot{S}_0 \qquad \text{(A5.21)}$$

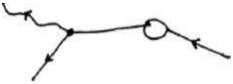
Combining the R.H.S. and the L.H.S. and comparing the coefficients of S_1, S_1, T and T_2 we obtain the working equations of motion given by eq. (5.2.13) in the text.

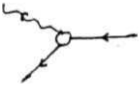
The second set of equations can be obtained in an identical fashion.

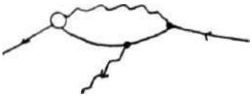
APPENDIX 5.3

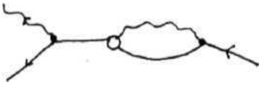
In this appendix we give the diagrams which result from the application of the MRTDCCM evolution operator to obtain the equations of motion. In these diagrams 0 represents the hamiltonian vertex and dot represents the evolution operator vertex. These diagrams are obtained using conventional diagrammatic techniques [31].











REFERENCES

1. I. Benjamin J. Chem. Phys. 85 5611 (1986).
2. B. Gazdy and D. A. Micha, J. Chem. Phys., **82**, 4926 (1985).
3. K. L. Sebastian, Phys. Rev. B, 32, 6976 (1985).
4. M. Durga Prasad, J. Chem. Phys., **88,** 7005 (1988).
5. S. Guha and D. Mukherjee, Chem. Phys. Lett.,**186**, 84 (1990).
6. H. Koppel , W. Domcke and L. S. Cederbaum, Adv. Chem. Phys., 57, 59 (1984).
7. K. F. Fread, Topics Appl. Phys., 15, 23 (1976).
8. R. L. Whitten, G. S. Ezra and G. R. Grant, Ann. Rev. Phys. Chem. 36, 277 (1985).
9. M. Desouter-Lecomte, D. Deherang, B. Leyh-NIhant, M. Th. Praet, A. J. Lorquet and J.C. Lorquet, J. Phys. Chem., **89**, 214 (1985).
10. U. Manthe and H. Koppel, J. Chem. Phys., S3, 1658 (1990);
11. U. Manthe and H. Koppel, Chem. Phys. Lett., **178,** 36 (1991).
12. R. Schneider and W. Domcke, Chem. Phys. Lett., **159** 61. (1989).
13. R. Schneider and W. Domcke, Chem Phys Lett, **150,** 235 (1988).
14. R. T. Skodje and D. G. Truhler, J. Chem. Phys., 80, 3123 (1984).
15. R. Schneider, W. Domcke and H. Koppel, J Chem Phys, **92**, 1045 (1990).
16. G. Stock and W. Domcke W, J. Chem. Phys., **93**, 5496 (1990)
17. G. Stock and W.H. Miller, Chem. Phys. Lett., **197**, 396 (1992).
18. H. Koppel, Chem. Phys., **77,** 359 (1983).
19. V. Domcke and H. Koppel, Chem. Phys. Lett., **140**, 133 (1987).
20. G. Stock and W. Domcke, Chem Phys. Lett., **124**, 227 (1988).
21. R. D. Coalson and J. L. Kinsey, J. Chem. Phys. 85, 4322 (1986).

22. S. I. Sawada, R. Heather, B. Jackson and H. Metiu, J. Chem. Phys, 83, 3009 (1985).

24. S. I. Sawada and H. Metiu, J. Chem. Phys., 84, 227 (1986); S. I. Sawada and H. Metiu, J. Chem. Phys., 84, 6293 (1986).

25. R. D. Coalson, J. Chem. Phys 86, 6823 (1987).

26. E. J. Heller, J. Chem. Phys., 75, 2923 (1981).

27. M. Durga Prasad, Chem. Phys. Lett. 194, 27 (1992).

28. Z. Kotler, A. Nitzan and R. Kosloff, Chem. Phys. Lett., 153, 483 (1988).

29. J. R. Waldeck, J. Campos-Martinez and R. D. Coalson, J. Chem. Phys. 94, 2773 (1991).

30. F. Brogli, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, A. S. Manocha, J. A. Pople and L. Radom Chem Phys 4, 107 (1974).

31. a)A. L. Fetter and J. D. Walecka, Quantum theory of many particle systems, McGraw-Hill, New York, 1971;b) D. J. Thouless, The Quantum mechanics of many body systems, Academic New York, 1961.

32. R. M. Wilcox, J. Math. Phys., 8, 962 (1967).

CHAPTER 6

CONCLUDING REMARKS

In this thesis, we have discussed the application of the infinite dimensional Lie-algebra to obtain the dynamics on anharmonic potential energy surfaces. While all the Lie-algebraic applications to date have used the finite dimensional Lie-algebras leading to a truncation in the potential energy surface in the hamiltonian, our methodology does not require a truncation in the hamiltonian [1-5]. The methodology is discussed in detail in chapter 2. Two ways of decomposing the algebra have been discussed leading to two different forms of the time evolution operator giving decoupled equations of motion. These two forms of the time evolution operator are found to be the time dependent generalisations of the CCM wave operators corresponding to the NCCM and the ECCM ansatz derived by Arponen [6]. The NCCM and ECCM versions developed by Arponen were tailored for the dynamics of states represented by a single reference state (treated as vacuum) at t=0. Although the extentions of NCCM to multireference states has been discussed by several authors [71, no extensions of the ECCM formalism to open shell systems have appeared to dateThe subsystem embedding condition has always been added as an additional sufficient condition to eliminate the operator redundancy in the open shell CCM theories. Our results on the other hand are different in the sense, the subsystem embedding condition emerges naturally in the algebraic theory. Secondly, it provides a natural extension of the ECCM theory to multireference states also.

We have made a limited study of the convergence properties of the TDCCM approach. Specifically, we studied the propagation of the harmonic oscillator ground state on several anharmonic potential energy surfaces and compared the results with the numerically converged basis set results. The applicability of the CCM for evaluating the ground state energy of the AHOs has been studied quite extensively over the past few years [8-13]. One of the major findings of these studies is that the CCM provides a rapid convergence (relative to a linear basis set expansion) upto a point [8]. We find a similar situation in the present time dependent context also. Second, Kaulfuss and Altenbokum [10] showed that the CCM wave functions in the boson representation are not always normalizable thus may not form part of any L^2 discretizable Hilbert space. While this aspect of the CCM is not satisfactory, it does not hinder the calculations of any physically relevant quantities such as expectation values since U can be replaced with U and Hausdorff expansion [14] provides a simple recipe to evaluate the resulting expression. Third, several authors noted the existence of multiple solutions for the CCM equations for the ground states [11,12]. In the context of the time dependent Schroedinger equation these additional roots have no direct role to play, since one integrates first order differential equations in time as an initial value problem. However, since the solution oscillates around the roots of the stationary state equations, these spurious roots might affect the stability of numerical integration. This could have been the case for our inability to integrate for long enough times for a few non-adiabatic systems discussed in chapter 5. Further work on the nature of such spurious roots might throw more light on their influence on the dynamics.

The advantages of the exponential ansatz from a computational point of view appear at two levels. Since the quantity of primary interest is cluster operator S = ln(U), we can expect a better convergence pattern because the logarithmic function changes more slowly than the linear function. We stress that the formalism developed in chapter 2 and the conclusions drawn here are general and are valid for any anharmonic system, because, as we have shown in chapter 2, all anharmonic systems with a given number of degrees of freedom belong to the same Lie-algebra. We also note that the wave function in the algebraic aproach receives contributions from *all* the basis functions in the Hilbert space because of its exponential structure. For example,

$$U_0 |0\rangle = \exp [\sum_m S_m a^{+m} |0\rangle]$$
$$= \exp(S_0) \{ |0\rangle + S_1 |1\rangle + (S_2 + S_1^2/2!) |2\rangle$$
$$+ (S_3 + S_1 S_2 + S_1^3 /3!) |3\rangle + \dots \}. \qquad (6.1)$$

Even when S is approximated by a finite number of operators, the series in (6.1) contains *all* the basis functions in the Hilbert space, though the coefficients of some of these basis functions are dependent on the coefficients of the lower functions. This greater flexibility in the definition of the underlying wave function encompassing the entire Hilbert space of the wave functions is at the origin of the faster convergence pattern exhibited by the algebraic approach. The algebraic approach required very few variables to describe the dynamics of the exponentially repulsive potential, the Morse potential and the atom-diatom collision in the classical path approximation [1-5] whilethe basis set approach requires (in principle) infinite number of variables (the coefficients of the basis functions in the Hilbert space such as the harmonic oscillator eigen-functions). All these coefficients of the basis functions are polynomial functions of the six Lie-algebraic parameters. These arguments carry over to anharmonic systems also. Second, for multidimensional systems, the size of the basis set required increases exponentially with the number of degrees of freedom in the system even when finite basis sets are used. On the other hand, number of cluster operators required to provide a numerically converged U increases only linearly with the number of degrees of freedom since S is the logarithm of U. These features make the algebraic approach particularly well suited for the description of dynamics on multidimensional anharmonic surfaces.

We have applied the TDCCM formalism to a few one and multidimensional systems to study its convergence properties in chapters 3,4 and 5. The calculations on the one dimensional systems, were carried out so that the results can be compared with those obtained from the basis set expansion approach. The one dimensional exponentially repulsive potential showed a faster convergence pattern than the basis set expansion method and the transition probabilities from the ground state to the higher eigenstates of the hamiltonian tallied well with the exact results. The calculations on the Morse potential energy surface showed similar trends. Vibrational transition probabilities were evaluated for the collision between an atom and a diatom and the results were found to very close to the exact even in the high energy region where the anharmonicities in the systems increase. Also, similar to the previous two applications the convergence obatined is faster than the basis set expansion approach. In the two dimensional systems discussed in chapter 4, the exponentially repulsive surface describing the photodissociation dynamics in the Beswick and Jortner model [16] showed a very good convergence pattern and a good agreement with the basis set expansion approach. While we were unable to carry out convergence studies on the Henon-Heils system, we found that for the more anharmonic system II, one of the problems of TDCCM, namely the norm violation, appearing.

In chapter 5 we have applied the coherent state algebra and TDCCM which corresponds to the GWP [14] in the coordinate space representation to study the non-adiabatic dynamics of a few model systems. Two different approaches were made. In the first of them, we have mapped the two state, n mode hamiltonian to a one state, n mode hamiltonian. We then used the GWP in the coherent state algebraic formalism to evaluate the dynamics. In systems with only one coupling mode, the GWP results were in good agreement with the converged basis set results when the coupling was weak. Similar trends were found for systems with several vibrational modes though the agreement was not good. Hoping to better the results we have carried out the calculations using TDCCM. The equations obtained were very stiff and we could not integrate the equations for sufficiently long times to obtain reasonable spectra. We then extended the TDCCM approach to multireference state situations (MRTDCCM) and used it to obtain the dynamics of the full two state, n mode hamiltonian. While we were unable to carry out convergence studies, the results at S_1 level of approximation did improve the results to some extent.

The stiffness of the equations and the norm violation encountered in certain systems can probably be overcome by shifting the coordinate system to a time dependent frame [17]. In this frame the new operators b and b^+ are related to the old creation and annihilation operators a. and a. transformation

$$b_i^+ = a_i^+ + C_i(t) \tag{6.2}$$

$$b_i = a_i + C_i^*(t) \tag{6.3}$$

The working equations of motion for corresponding to the old set of operators given by

$$i\dot{S}(m) = \langle m \mid \bar{H} \mid 0\rangle \tag{6.4}$$

are now modified to

$$i(\dot{S}_n + \dot{C}\,\dot{S}_{n+1}) = \langle n \mid \bar{H} \mid 0\rangle \tag{6.5}$$

where H is the effective hamiltonian and S_n are the cluster amplitudes in the time dependent frame. The additional equation on C can be used to decouple S from S leading to the classical equations of motion for the C coefficients. In this time dependent coordinate frame, the wave packet moves along its centroid in time. The potential is now expanded locally which reduces the effect of the global anharmonicities on the wave packet. Therefore, we expect the distortions in the wave packet to be less. In the absence of these distortions, the stiffness of the working equations may minimise.

REFERENCES

1. (a) B. Gazdy and D.A. Micha, J. Chem. Phys., 82, 4926(1985).;(b) D.A. Micha Int. J. Quantum Chem.,23, 551(1983);(c) E.Vilallonga and D.A.Micha, Int.J.Quantum Chem. Symp,15, 653(1981);(d) idem, J.Chem. Phys.,rg, 3794(1983). (e). J.A. Recamier, D.A. Micha and B. Gazdy, Chem. Phys. Lett., **119**, 383 (1985); (f) J. Echave, F.M. Fernandez and D. A. Micha, J. Chem. Phys., 94, 3537 (1991); (g) J. A. Recamier, D.A. Micha and B. Gazdy, J. Chem. Phys., 85, 5093 (1986).
2. I. Benjamin, J. Chem. Phys., 85, 5611(1986).
3. a) H.K. Shin, Chem. Phys. Lett., 3, 125(1969);b) idem J. Chem Phys. 81, 220 (1981).
4. Y. Alhassid and R. D. Levine, J. Chem. Phys., 67, 4321(1977).
5. J.Yuan and R. Gilmore, J. Chem. Phys., 86, 130(1987).
6. J. Arponen, Ann. Phys., 151, 311 (1983); R.F. Bishop, J. Arponen and E. Pajanne, Lecture notes in chemistry Vol.50 edited by D. Mukherjee p.79 (Springer, Berlin 1989).
7. R. Chowdary, D. Mukherjee and M. Durga Prasad, in Lecture notes in Chemistry Vol. 50 edited by D. Mukherjee p.3 (Springer, Berlin 1989); D. Mukherjee and S. Pal, Adv. Quantum Chem., 20, 292 (1989).
8. H. G. Kummel, Condensed Matter Theories, Vol. 3 edited by J. S. Arponen, R. F. Bishop and M. Manninen, p.21 (Plenum press, New York 1988).
9. C.S.Hsue and J.L. Chern, Phys. Rev. D, 29, 643 (1984).
10. U.B. Kaulfuss and M. Altenbokum, Phys. Rev. D, 33, 3658 (1986).

11. R.F. Bishop, M.C. Bosca and M.F. **Flynn, Phys**. Rev, A, 40, 3484 (1989); R.F. Bishop and M.F. Flynn, Phys. Rev. A, 38, 2211 (1988)

12. R. F. Bishop, M.C. Bosca and M.F. Flynn, Phys. Lett. A, 132, 440 (1988).

13. J. **Arponen**, R.F. Bishop and E. **Pajanne**, Phys. Rev. A, 36, 2519, 2539 (1987).

14. R. M. Wilcox, J. Math. Phys., **8, 962** (1967).

15. E. J. Heller, **Acc**. **Chem**. Res, 14, 386(1981).

16. J. A. Beswick and J. **Jortner, Chem**. Phys., **24, 1** (1977).

17. M. Durga **Prasad**, Lecture notes in chemistry, Vol. 50, edited by D. **Mukherjee**, p 321 (Springer, Berlin 1989).

LIST OF PUBLICATIONS

1) Some aspects of the Lie-algebraic description of anharmonic dynamics"; G. Madhavi Sastry and M. Durga Prasad, Theor. chim. acta (submitted).

2) "A gaussian wave packet propagation study of non-adiabatic dynamics"; G. Madhavi Sastry and H. Durga Prasad, Proc. Indian Acad. Sci. (Chem. Sci.) (in press).

3) "The tine dependent coupled cluster approach to Molecular photodissociation dynamics"; G. Madhavi Sastry and M. Durga Prasad, Chem. Phys. Lett. (submitted).