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,

\[ H = \sum_i h_i, \quad (1) \]

\[ [h_i, h_j] = \sum_k C_{ij}^k h_k, \quad (2) \]

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

\[ U = \exp(X), \quad (3) \]

\[ X = -X^\dagger = \sum_i x_i h_i. \quad (4) \]

Here the coefficients \(C_{ij}\) 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

\[ i U^{-1} U = U^{-1} H U . \quad (5) \]

Expanding both sides of eq.(5) by the Hausdorff expansion [2] and equating the coefficients of each \( h_i \) 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 necessitating further approximations. In addition, under some exotic conditions, the existence of the solution is also questionable.

These problems can be surmounted by parametrizing the evolution operator in a non-canonical product of exponential operators. Vie and Norman [1] and Wolf and Korsch [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 sub-algebra. 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 time 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] 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 a reduction principle eliminates both the problems encountered in the construction of the anharmonic 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

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

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

$$L_0 = \{ Q_{mn}, q^m p^n : 0 \leq m, n < \infty \}$$

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

$$L_0 = \{ A_{mn}, a^m a^n : 0 \leq m, n \leq \infty \}$$

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

$$U = \prod \exp [ S_{mn} a^m a^n ]$$
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

\[ C_k = \{ a^{+(k+n)} a_k \mid n \geq 1 \} \quad 0 \leq k \leq \infty \] (10a)

b. Sets of annihilation operators

\[ A_k = \{ a^{+k} a^{k+n} \mid n \geq 1 \} \quad 0 \leq k \leq \infty \] (10b)

c. Sets of diagonal operators

\[ D_k = \{ a^{+k} a^k \} \quad 0 \leq k \leq \infty \] (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,

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

\[ W_k \in C_k, \quad Z_k \in D_k, \quad Y_k \in A_k \quad (11a) \]

\[ W_k = \sum_{m} S_{mk} a^{+(m+k)} a^k, \quad Y_k = \sum_{m} y_{mk} a^{+k} a^{(m+k)}, \quad Z_k = \sum_{m} S_{mk} a^{+k} a^k \]

where \( m > k > 0 \) and

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

\[ W_k \in C_k, \quad Y_k \in A_k, \quad Z_k \in D_k \quad (12b) \]

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

\[ U = U_0 U_1 U_2 \ldots \quad (13a) \]

\[ U_0 = \exp \left[ \sum_{n_1, n_2} S_{n_1 n_2}^0 \left( a_1^+ \right)^{n_1} \left( a_2^+ \right)^{n_2} + S_{00}^0 \right] \quad (13b) \]

\[ U_1 = \exp \left[ \sum_{\alpha} \sum_{n_1, n_2} S_{n_1 n_2}^1 \left( a_1^+ \right)^{n_1} \left( a_2^+ \right)^{n_2} a_\alpha \right] \exp \left[ \sum_{\alpha, \beta} S_{\alpha \beta}^1 a_\alpha^+ a_\beta \right] \quad (13c) \]

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 be written as [20]

\[
H = \sum_i |e_i \rangle \langle e_i| + \omega_c a_c^+ a_c + \sum_i |e_i \rangle \langle V_c (a_c^+ + a_c) | e_i \rangle \\
+ \sum_t \omega_t a_t^+ a_t + \sum_i |e_i \rangle \langle V_t^{(i)} [a_t^+ + a_t] \rangle e_i \rangle 
\]

(14)

where, \( \omega \) 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. \( \varepsilon \) is the energy of the ith electronic state \( e_i \). \( a \) and \( a^\dagger \) are the boson ladder operators operative in the vibrational subsystem. Defining the auxiliary parameters,

\[
V_t = 0.5 (V_t^{(1)} + V_t^{(2)}) 
\]

(15a)

\[
U_t = 0.5 (V_t^{(1)} - V_t^{(2)}) 
\]

(15b)

the resultant Hamiltonian turns out to be

\[
\tilde{H}_t = \sum_{n=t,c} \omega_n a_n^+ a_n + \sum_t V_t (a_t^+ + a_t) - \varepsilon \cos(\pi \sum_c a_c^+ a_c) \\
- \sum_t U_t (a_t^+ + a_t) \cos(\pi \sum_c a_c^+ a_c) + V_c (a_c^+ + a_c) 
\]

(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

\[
\mathcal{L}_n = \{ 1, a_i^+, a_i, a_i^+ a_j^+, a_i a_j, a_i^+ a_j \} 
\]

(17)
Since we are particularly interested in the dynamics of the vacuum state, the evolution operator was parametrised as

\[ U = \exp \left( \sum_{i} S_{1}^{i} a_{i}^{+} + \sum_{i \leq j} S_{2}^{i} a_{i}^{+} a_{j}^{+} \right) \exp \left( - \sum_{i} T_{1}^{i} a_{i} - \sum_{i \leq j} T_{2}^{i} a_{i} a_{j} \right) X \exp \left[ S_{0} \right] \] (18)

As the annihilation operators are to the extreme right the equations for the autocorrelation function simplify. The term \( U \cos(n a a) U \) which results from the multicommutator expansion of \( U H U \) can be rearranged as \( \exp(Xa) \cos(na a) \exp(Ya) \) or \( \exp(Xa) \exp(Ya) \cos(na a) \) 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 whereas 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 were in reasonably good agreement with the exact.

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

\[ U \cdot \exp[ S_{m} a_{m}^{+} ] \] (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 whereas 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

\[ L = \{ |i> <k| ; \prod a_\alpha^{+ m_\alpha} a_\alpha^{n_\alpha} \} \forall i, k ; 0 \leq m_\alpha, n_\alpha \leq \infty \]  

(20)

In the case of MRTDCCM1 the operators \(|i> <k|\) correspond to the electronic state subsystem and \(a_\alpha^{+}\) and \(a_\alpha\) 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 operators 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.
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