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Some aspects of the algebraic description of anharmonic dynamics

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Summary. A formally exact Lie-algebraic description of the dynamics on anharmonic potential energy surfaces is developed. The anharmonic hamiltonians belong to infinite dimensional Lie-algebras. Two ways of decomposing the algebras in the boson representation are presented. The evolution operator resulting from these two methods, which differ in the ordering of the boson operators, is shown to correspond to the time dependent generalizations of normal coupled cluster method (NCCM) and the extended coupled cluster method (ECCM). Relative merits of the two approaches are discussed. The NCCM formalism is applied to calculate the $0 \rightarrow n$ vibrational transition probabilities of an exponentially perturbed harmonic oscillator modeling the collinear inelastic collision of $He + H_2$ system. Good agreement with the basis set expansion approach is obtained with the Lie-algebraic approach showing a better convergence pattern.

Key words: Infinite dimensional Lie-algebra – Coupled cluster method

1 Introduction

Dynamics of nonstationary states on anharmonic potential surfaces plays a major role in several processes of chemical interest. 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 [2–16].

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

$$H = \sum_i h_i l_i, \tag{1.1a}$$

$$[l_i, l_j] = \sum_k C_{ij}^k l_k, \tag{1.1b}$$

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

$$U = \exp(X), \tag{1.2a}$$

$$X = -X^{+} = \sum_{i} x_i l_i. \tag{1.2b}$$

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 (1.2a) into Schroedinger's equation. The resulting expressions are compact and provide a convenient route for generating the solution either perturbatively as is done in Magnus expansion [16] or nonperturbatively [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 (Ref. [2(f)]) in which the convergence pattern of the time dependent wave function is improved compared to that in the conventional basis set expansion approach.

In this paper 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 Sect. 2 along with a discussion on the difficulties encountered when a canonical representation of the evolution operator such as Eq. (1.2) is invoked. Briefly, these consist of the following: Since the algebra is infinite dimensional, the number of independent variables required to parametrize the evolution operator is also infinity. Consequently, truncations are necessary in any practical calculation. Even then, the governing equations for the generators of the evolution operator contain infinite order polynomials of the unknown coefficients necessitating further approximations. In addition, under some exotic conditions, the existence of the solution is also questionable [16].

These problems can be surmounted by parametrizing the evolution operator in a noncanonical 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 subalgebra. More recently this reduction principle was extended to algebras which have only noninvariant subalgebras by Sreelatha and Prasad [20]. This reduction principle is reviewed in Sect. 2.1. We then use it to construct the time evolution operator for a general 1-d anharmonic oscillator in Sect. 2.2.

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 [24] of the ansatz postulated by the coupled cluster method (CCM) [24–32] for the anharmonic oscillators [33–38]. The concepts invoked in the CCM such as the cluster decomposition property [25] and the subsystem embedding condition [28] 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 Sect. 2.3.

As the number of variables required to describe the system by the algebraic approach is infinity, truncations are necessary in any practical calculation just as in the case of basis set expansions. In Sect. 3 we use the algebraic approach to follow the dynamics of an exponentially perturbed harmonic oscillator with a view to understand its convergence behaviour. It turns out that, at least for this system, the algebraic approach has a better convergence behaviour than the corresponding basis set expansion approach. As we noted earlier, all the anharmonic hamiltonians belong to the same Lie-algebra. Thus we expect these trends to be more general. Finally, in the last section, we conclude with a general discussion of the method.

2 Methodology

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

$$H = p^2/2m + \sum_{n=0} (1/n!) V_n q^n. \tag{2.1a}$$

Here q and p are the coordinate and the momentum operators of the particle, m is the mass and V_n 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

$$L_0 = \{Q_{mn} = q^m p^n;\ 0 \leqslant m, n \leqslant \infty\} \tag{2.2a}$$

(unless the summation in Eq. (2.1a) is restricted to at most quadratic terms). Transforming to the harmonic oscillator ladder operator representation, we have

$$H = \sum_{m,n} h_{mn} a^{+m} a^n. \tag{2.1b}$$

Here a^+ and a are the usual harmonic oscillator ladder operators. In this representation L_0 is given by

$$L_0 = \{A_{mn} = a^{+m} a^n;\ 0 \leqslant m, n \leqslant \infty\}. \tag{2.2b}$$

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

$$U = \exp[S], \tag{2.3}$$

$$S = \sum_{m,n=0}^{\infty} S_{mn} a^{+m} a^n; \qquad S_{mn} = -S_{nm}^*. \tag{2.4}$$

This representation runs into two difficulties. To begin with, even when the summation for S operator in Eqs. (2.3) and (2.4) is restricted to some finite values of m and n ($m, n \geqslant 2$), the Hausdorff expansion gives a nonterminating series. Since little is known about the magnitudes of S_{mn} *a priori*, it becomes difficult to evaluate them numerically without invoking some further approximations. The second problem with the representation (2.3), (2.4) is that under some conditions the governing equations are not well defined [16].

Both these problems arise because the ansatz (2.3), (2.4) treats stepup and stepdown operators on equal footing. As a consequence, the multicommutator expansion becomes a nonterminating series. If these two sets of operators are disentangled and written as separate exponentials these difficulties would not appear. This provides the motivation for invoking a Wei–Norman product form for the evolution operator. In Sect. 2.1 we discuss a reduction principle by which such a disentanglement of operators can be achieved in a systematic fashion by exploiting the subalgebra structure of L_0 and in Sect. 2.2 we will use it to construct the evolution operator for the 1-d anharmonic oscillators. Extensions to multidimensional AHOs will be presented in Sect. 2.3.

2.1 Reduction principle and decoupling of algebraic evolution operator

In this 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_0 containing the hamiltonian H has a subalgebra L_1 spanned by the operator set $\{l_i^1\}$ and define C_0 as the difference of L_0 and L_1

$$C_0 = \{l_i^0\} = L_0 - L_1 \subset L_0. \tag{2.5a}$$

If U is parametrized as

$$U = U_0 U_R, \tag{2.5b}$$

$$U_0 = \exp(X_0), \tag{2.5c}$$

$$X_0 = \sum_i x_i^0 l_i^0; \quad l_i^0 \in C_0, \tag{2.5d}$$

the governing equation for U_R is obtained by substituting Eq. (2.5b) in the TDSE and is given by

$$i\dot{U}_R = H_R U_R, \tag{2.6a}$$

$$H_R = U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0. \tag{2.6b}$$

Note that by Eq. (2.6), U_R is generated by the effective hamiltonian H_R. Thus an exponential representation of U_R is generated by the operator basis of the algebra to which H_R belongs. In general, H_R belongs to L_0. However it is possible to restrict H_R to L_1, by requiring that all the coefficients of the l_i^0 operators in H_R vanish. With this, it would now be possible to parametrize U_R strictly in terms of the operators of L_1 alone. Since C_0 does not contain any of the operators belonging to L_1, 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_i^0 variables is equal to the number of operators l_i^0 in C_0 by definition (Eq. (2.5d)), these equations can always be satisfied. Formally this can be written as

$$(U_0^{-1} H U_0 - \mathrm{i} U_0^{-1} \dot{U}_0)_{l_i^0} = 0, \tag{2.6c}$$

which becomes the working equation for $\dot{U}_0$. With Eq. (2.6c) satisfied and consequently H_R restricted to L_1, U_R can now be parametrized as

$$U_R = \exp(X_1) \tag{2.6d}$$

$$X_1 = \sum_i x_i^1 l_i^1, \quad l_i^1 \in L_1. \tag{2.6e}$$

Note that to solve Eq. (2.6e) for x_i^0 coefficients, no knowledge of the x_i^1 coefficients is needed. Thus, the two sets of equations for x_i^0 and x_i^1 coefficients are decoupled from each other. The result of Eqs. (2.5)–(2.6) can easily be generalized to a situation when L_0 has a sequence of subalgebras L_k such that $L_0 \supseteq L_1 \supseteq L_2 \ldots$ The evolution operator can be factorized as

$$U = \prod_k U_k, \tag{2.7a}$$

$$U_k = \exp(X_k), \tag{2.7b}$$

$$X_k = \sum_k x_i^k l_i^k; \quad l_i^k \in C_k = L_k - L_{k+1}. \tag{2.7c}$$

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

$$(U_k^{-1} \bar{H}_k U_k - \mathrm{i} U_k^{-1} \dot{U}_k)_{l_i^k} = 0, \tag{2.8}$$

$$\bar{H}_k = U_{k-1}^{-1} \bar{H}_{k-1} U_{k-1} - \mathrm{i} U_{k-1}^{-1} \dot{U}_{k-1}. \tag{2.9}$$

2.2 *Evolution operator for one dimensional AHO*

We now turn to the construction of the evolution operator of a one dimensional anharmonic oscillator. There are several ways in which L_0 (Eq. (2.2b)) can be decomposed as envisaged in Sect. 2.1. These correspond to different variants of the CCM ansatz [24]. We discuss two versions here. It is convenient for this purpose to classify the operators in L_0 as follows:

(a) *Sets of creation operators*

$$C_k = \{a^{+(k+n)} a^k; \, n \geqslant 1\}, \quad 0 \leqslant k \leqslant \infty; \tag{2.10a}$$

(b) *Sets of annihilation operators*

$$A_k = \{a^{+k}a^{k+n};\ n \geqslant 1\},\quad 0 \leqslant k \leqslant \infty; \tag{2.10b}$$

(c) *Sets of diagonal operators*

$$D_k = \{a^{+k}a^{k}\},\quad 0 \leqslant k \leqslant \infty. \tag{2.10c}$$

Consider now the set of operators $L_1 = L_0 - C_0$. Other than the identity operator in D_0, all other operators in this set contain *at least* one annihilation operator. Consequently, their commutators also contain at least one annihilation operator. Thus L_1 is closed under commutation and hence is a Lie-algebra. Consequently, the time evolution operator can be factorized as

$$U = U_0 U_{\mathrm{R}}, \tag{2.11a}$$

where U_0 and U_{R} are exponential operators generated by the operators in C_0 and L_1, respectively,

$$U_0 = \exp\left[\sum_m S_{m0}a^{+m}\right], \tag{2.11b}$$

$$U_{\mathrm{R}} = \exp\left[\sum_m r_m X_m\right],\quad X_m \in L_1. \tag{2.11c}$$

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

$$U_{\mathrm{R}} = U_{D0}U_{\mathrm{R}}', \tag{2.11d}$$

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

$$U_{D0} = \exp(S_{00}), \tag{2.11e}$$

$$U_{\mathrm{R}}' = \exp\left[\sum_m r_m' X_m'\right],\quad X_m' \in L_1' \tag{2.11f}$$

As per the discussion in Sect. 2.1, the working equations for the coefficient set S_{m0} would be decoupled from the rest of the variables S_{00} and r_m'. Similarly, equation for S_{00} depends upon S_{m0} parametrically, but does not depend upon r_m'. Thus at the first stage U is factorized into three terms as follows:

$$U = U_0 U_{D0} U_{\mathrm{R}}'. \tag{2.11g}$$

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 subalgebras of $L_k\}\quad L_k'$ for all k. The last set in this sequence of subalgebras is

$$L_\infty = \bigcup_{k=1} A_k. \tag{2.12a}$$

This can be further decomposed as follows:

$$L_1'' = L_\infty - A_0, \tag{2.12b}$$

$$L_{k+1}'' = L_k'' - A_k. \tag{2.12c}$$

Thus the evolution operator after complete factorization reads as

$$U = \prod_{k=0} [\exp(W_k)\exp(Z_k)] \prod_{l=0} \exp(Y_l), \quad W_k \in C_k,\ Z_k \in D_k,\ Y_l \in A_l, \quad (2.13)$$

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

where $m > k \geqslant 0$.

In the CCM parlance, this ansatz corresponds to the normal coupled cluster method (NCCM) [24].

Returning to the equation of motion for U_0,

$$(U_0^{-1} H U_0 - \mathrm{i}\, U_0^{-1} \dot{U}_0)_{l_i^0} = 0, \quad (2.14a)$$

we find

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

$$= \mathrm{i}\, \mathrm{d}/\mathrm{d}t + \mathrm{i} \sum \dot{S}_{m0} a^{+m}, \quad (2.14b)$$

since the remaining terms in the Hausdorff expansion are zero. Note that $\dot{S}_{m0}$ 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,

$$U_0^{-1} H U_0 = H + \sum S_{m0}[H, a^{+m}] + 1/2! \sum S_{m0} S_{n0} [[H, a^{+m}], a^{+n}] + \ldots \quad (2.14c)$$

we note that the creation operators in H can be taken out as they commute with a^{+m} 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 nonzero commutator. Thus the working equations would contain polynomial terms in S_{m0}, no higher than kth power. This argument is easily generalized to show that the rest of the terms in U such as U_1, U_2 etc., are also free from these two defects unlike the canonical representation Eq. (1.2).

The advantages of the ansatz (2.12) are best demonstrated in the context of the evolution of harmonic oscillator eigenstates. Consider as a first example, the evolution of the vacuum state,

$$U|0\rangle = \exp\left[\sum_m S_{m0} a^{+m} + S_{00}\right]|0\rangle, \quad (2.15a)$$

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

$$U|1\rangle = \exp\left[\sum_{m=1} S_{m0} a^{+m} + S_{00}\right] \exp\left[\sum_{m=2} S_{m1} a^{+m} a\right] \exp[S_{11} a^{+} a]|1\rangle. \quad (2.15b)$$

Here the S_{m0} matrix elements remain frozen from the previous calculation for the evaluation of the vacuum state by Eq. (2.14). Thus depending upon the state to be propagated U is automatically restricted.

A second sequence of subalgebras to L_0 which yield the evolution operator corresponding to the so-called extended coupled cluster method (ECCM) [24] is obtained as follows:

$$L_1 = L_0 - C_0, \tag{2.16a}$$

$$L_1' = L_1 - A_0, \tag{2.16b}$$

$$L_1'' = L_1' - D_0, \tag{2.16c}$$

$$L_k = L_{k-1}'' - C_{k-1}, \tag{2.17a}$$

$$L_k' = L_k - A_{k-1}, \tag{2.17b}$$

$$L_k'' = L_k' - D_{k-1}. \tag{2.17c}$$

The evolution operator is given by

$$U = \prod_{k=0} [\exp(W_k)\exp(Y_k)\exp(Z_k)]; \quad W_k \in C_k,\ Y_k \in A_k,\ Z_k \in D_k. \tag{2.18}$$

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

$$U|0\rangle = \exp\left[\sum_m S_{m0} a^{+m}\right] \exp\left[\sum_m y_{0m} a^m\right] \exp(S_{00})|0\rangle. \tag{2.19}$$

The equations of motion for the different cluster amplitudes S_{m0} are obtained from Eq. (2.8). 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. (2.13) for NCCM

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

$$\times \prod_{k=0}^{m} [\exp(W_k)\exp(Z_k)] \prod_{l=0}^{m} \exp(Y_l)|m\rangle. \tag{2.20}$$

The corresponding expression for ECCM is given by

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

$$\times \prod_{k=0}^{m} [\exp(W_k)\exp(Y_k)\exp(Z_k)]\,|m\rangle. \tag{2.21}$$

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 state. 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.

2.3 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

$$H = \sum_{i \leqslant j=1}^{D} p_i p_j / 2m_{ij} + \sum V_i^{(1)} q_i + 1/2! \sum_{i \leqslant j} V_{ij}^{(2)} q_i q_j + \ldots \tag{2.22a}$$

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

$$L_0 = \left\{ \prod_{i=1}^{D} q_i^{n_i} p_i^{m_i};\ 0 \leqslant n_i, m_i \leqslant \infty \right\} \tag{2.23a}$$

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

$$H = \sum_{m_i, n_i = 0}^{\infty} h(m_1 n_1\ m_2 n_2\ \ldots\ m_D n_D) \prod_{\alpha} a_\alpha^{+\, m_\alpha} a_\alpha^{n_\alpha}, \tag{2.22b}$$

$$L_0 = \left\{ \prod_{\alpha=1}^{D} a^{+\, m_\alpha} a^{n_\alpha};\ 0 \leqslant m_\alpha, n_\alpha \leqslant \infty \right\}. \tag{2.23b}$$

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

$$C_0 = \left\{ \prod a_\alpha^{+\, n_\alpha};\ 0 \leqslant n_\alpha \leqslant \infty \right\}, \tag{2.24a}$$

$$D_0 = \{1\}, \tag{2.24b}$$

$$L_1' = \left\{ \prod_{\alpha=1}^{D} a_\alpha^{+\, n_\alpha} a_\beta;\ 0 \leqslant n_\alpha \leqslant \infty \right\}. \tag{2.24c}$$

With this, U can be parametrized as

$$U = U_0 U_1 U_2 \ldots, \tag{2.25a}$$

$$U_0 = \exp\left[\sum_{n_1 n_2 \ldots} S^0_{n_1 n_2 \ldots} (a_1^+)^{n_1} (a_2^+)^{n_2} \ldots + S^0_{00} \right], \tag{2.25b}$$

$$U_1 = \exp\left[\sum_{\alpha} \sum_{n_1 n_2 \ldots} S^1_{n_1 n_2 \ldots ; \alpha} (a_1^+)^{n_1} (a_2^+)^{n_2} \ldots a_\alpha \right] \exp\left[\sum_{\alpha\beta} S^1_{\alpha\beta} a_\alpha^+ a_\beta \right], \tag{2.25c}$$

etc. The only complication that arises is that the operators in the diagonal sets lead to nonterminating series and unlike in the one dimensional problem where each D_k contains only one element, these series 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 series. Thus U_1 of Eq. (2.37c), for example, would be given by

$$U_1 = \exp\left[\sum_{\alpha} \sum_{n_1 n_2 \ldots} S^1_{n_1 n_2 \ldots;\alpha}(a_1^+)^{n_1}(a_2^+)^{n_2} \ldots a_\alpha\right]\left[\sum_{\alpha,\beta} U'_{\alpha\beta} a_\alpha^+ a_\beta\right] \quad (2.25d)$$

3 Model applications

In order to demonstrate the power of the algebraic approach we have studied the dynamics of the harmonic oscillator ground state governed by an exponentially perturbed harmonic potential. The hamiltonian of the system [22] is given by

$$H = \hbar\omega a^+ a + F(t)\exp[Z(a^+ + a)], \quad (3.1a)$$

where

$$F(t) = E\,\mathrm{Sech}^2[(E/2m)^{1/2} t/a] \quad (3.1b)$$

and

$$Z = (\gamma/a)\sqrt{(\hbar/(2M\omega))}. \quad (3.1c)$$

This hamiltonian was used extensively in the past to model the inelastic scattering between an atom and a diatom in the collinear classical path approximation [21, 2, 5, 6, 8]. In that context E is the total energy of the collision system. Since microscopic reversibility is lost in the classical path approximation, it is customary to define E as [2, 5]

$$E = (1/8)m(v_f + v_i)^2. \quad (3.2)$$

Here v_f and v_i 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. γ and a characterize the interaction strength. In all the previous algebraic studies [2–8] this hamiltonian was truncated up to second order to make it an element of the harmonic oscillator algebra. We do not invoke this approximation here. The parameters of the system were chosen such that it corresponds to He–H_2 system [2] and the collision energy was varied in the range $2\hbar\omega \leqslant E \leqslant 20\hbar\omega$. Since we were interested in the dynamics of vacuum state only, the evolution operator takes the form

$$U_0 = \exp\left[\sum_{n=1}^{N} S_n(a^+)^n + S_0\right]. \quad (3.3)$$

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 working equations are obtained from Eq. (2.14a) by invoking the Hausdorff expansion. For example the equations for S_0 and S_1 are

$$i\dot{S}_0 = \tfrac{1}{2}\hbar\omega + Y_0, \tag{3.4}$$

$$i\dot{S}_1 = S_1\hbar\omega + Y_0 Y_1, \tag{3.5}$$

where

$$Y_0 = F(t)\exp(Z^2/2)\exp\left(\sum_{n=1} S_n Z^n\right), \tag{3.6}$$

$$Y_1 = Z + \sum_{n=2} S_n{}^n C_1 Z^{n-1}. \tag{3.7}$$

As an initial step we studied the sensitivity of S-matrix elements on the truncation index N in Eq. (3.3). The results of these studies are presented in Table 1 for $E = 7\hbar\omega$ and $20\hbar\omega$. From the table, it is apparent that the cluster amplitudes are fairly insensitive to the truncation index after about $N \geqslant 4$.

The transition probabilities from $0 \rightarrow 0, 1, 2, 3$ for some representative energies as a function of N are presented in Table 2. As can be seen, these are also insensitive to the truncation index for $N \geqslant 4$.

Lastly, in Table 3, we present $0 \rightarrow n$ transition probabilities for several energies with $N = 7$. We have also calculated the transition probabilities by expanding the wave function as a linear superposition of harmonic oscillator basis functions. In most cases, the algebraic results converge to the exact value by about S_4 while the calculation based on basis set expansion required upto 40 functions for convergence. These results indicate that the Lie-algebraic approach has a far better

Table 1. S-matrix elements at the end of the time development for different values of truncation index N

N	S_n					
n	2	3	4	5	6	7
$E = 7\hbar\omega$						
0	−0.7183[a]	−0.7215	−0.7214	−0.7214	−0.7214	−0.7214
	−0.4109E + 2[b]	−0.4108E + 2	−0.4108E + 2	−0.4108E + 2	−0.4108E + 2	−0.4108E + 2
1	−0.6680E − 1	−0.7356E − 1	−0.7342E − 1	−0.7342E − 1	−0.7342E − 1	−0.7342E − 1
	−0.1180E + 1	−0.1190E + 1	−0.1190E + 1	−0.1190E + 1	−0.1190E + 1	−0.1190E + 1
2	−0.9601E − 2	−0.8224E − 2	−0.8177E − 2	−0.8183E − 2	−0.8183E − 2	−0.8183E − 2
	−0.6982E − 2	−0.7845E − 2	−0.7836E − 2	−0.7832E − 2	−0.7832E − 2	−0.7832E − 2
3		0.1671E − 4	−0.1273E − 1	−0.1525E − 4	−0.1501E − 2	−0.1499E − 2
		0.7837E − 4	0.1073E − 3	0.1046E − 3	0.1044E − 3	0.1044E − 3
4			0.4216E − 6	0.1421E − 5	0.1499E − 5	0.1484E − 5
			−0.1162E − 5	−0.1722E − 5	−0.1593E − 5	−0.1587E − 5
5				−0.2177E − 7	−0.5331E − 7	−0.5479E − 7
				0.2703E − 8	0.8326E − 8	0.2900E − 8
6					0.2800E − 9	0.1124E − 8
					0.6366E − 9	0.7951E − 9
7						0.1183E − 10
						−0.2445E − 10

Table 1. (Continued)

N	S_n					
n	2	3	4	5	6	7
$E = 20\hbar\omega$						
0	−0.4346E + 1	−0.4389E + 1	−0.4393E + 1	−0.4393E + 1	−0.4393E + 1	−0.4393E + 1
	−0.4847E + 2	−0.4832E + 2	−0.4832E + 2	−0.4832E + 2	−0.4832E + 2	−0.4832E + 2
1	−0.4089	−0.4964	−0.4931	−0.4919	−0.4921	−0.4921
	−0.2747E + 1	−0.2808E + 1	−0.2814E + 1	−0.2813E + 1	−0.2813E + 1	−0.2813E + 1
2	−0.5806E − 1	−0.4670E − 1	−0.4337E − 1	−0.4392E − 1	−0.4404E − 1	−0.4400E − 1
	−0.4255E − 1	−0.5553E − 1	−0.5396E − 1	−0.5331E − 1	−0.5344E − 1	−0.5346E − 1
3		−0.4350E − 4	−0.4858E − 3	−0.6531E − 3	−0.5946E − 3	−0.5869E − 3
		0.81216E − 3	0.1333E − 2	0.1158E − 2	0.1116E − 2	0.1134E − 2
4			0.1571E − 4	0.4254E − 4	0.4898E − 4	0.4374E − 4
			−0.1145E − 4	−0.2511E − 4	−0.1210E − 4	−0.1041E − 4
5				−0.6453E − 6	−0.1754E − 5	−0.1864E − 5
				−0.7009E − 6	−0.5473E − 6	−0.1332E − 5
6					−0.6756E − 8	0.2397E − 7
					0.6637E − 7	0.7282E − 7
7						0.2539E − 8
						−0.2812E − 8

[a] Real part of S
[b] Imaginary part of S

Table 2. Transition probabilities $0 \rightarrow 0, 1, 2, 3$ as a function of the truncation index N

N Energy	2	3	4	5	6	7
4	0.7544[a]	0.7538	0.7538	0.7538	0.7538	0.7538
	0.1404[b]	0.1415	0.1415	0.1415	0.1415	0.1415
	0.2764E − 2[c]	0.2791E − 2	0.2791E − 2	0.2791E − 2	0.2791E − 2	0.2791E − 2
		0.8219E − 6[d]	0.8221E − 6	0.8221E − 6	0.8221E − 6	0.8221E − 6
10	0.4742E − 1	0.4659E − 1	0.4659E − 1	0.4659E − 1	0.4659E − 1	0.4659E − 1
	0.1666	0.1680	0.1680	0.1680	0.1680	0.1680
	0.2431	0.2495	0.2493	0.2493	0.2493	0.2493
		0.1941	0.1939	0.1939	0.1939	0.1939
16	0.1496E − 2	0.1418E − 2	0.1414E − 2	0.1415E − 2	0.1415E − 2	0.1415E − 2
	0.1132E − 1	0.1120E − 1	0.1119E − 1	0.1119E − 1	0.1119E − 1	0.1119E − 1
	0.4038E − 1	0.4126E − 1	0.4125E − 1	0.4125E − 1	0.4125E − 1	0.4125E − 1
		0.9377E − 1	0.9370E − 1	0.9370E − 1	0.9370E − 1	0.9370E − 1
20	0.1676E − 3	0.1538E − 3	0.1525E − 3	0.1527E − 3	0.1527E − 3	0.1527E − 3
	0.1644E − 2	0.1594E − 2	0.1588E − 2	0.1588E − 2	0.1588E − 2	0.1588E − 2
	0.7816E − 2	0.7910E − 2	0.7898E − 2	0.7897E − 2	0.7897E − 2	0.7897E − 2
		0.2499E − 1	0.2497E − 1	0.2497E − 1	0.2497E − 1	0.2497E − 1

[a, b, c] and [d] represent $0 \rightarrow 0$, $0 \rightarrow 1$, $0 \rightarrow 2$ and $0 \rightarrow 3$ transition probabilities, respectively

Table 3. Transition probabilities for H_2 (m) + He → H_2 (n) + He

$m \rightarrow n$ Energy ($\hbar\omega$ units)	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$	$0 \rightarrow 3$	$0 \rightarrow 4$	$0 \rightarrow 5$	$0 \rightarrow 6$	$0 \rightarrow 7$	$0 \rightarrow 8$	$0 \rightarrow 9$	$0 \rightarrow 10$
2.0	0.9896[a]	0.7875E − 3									
	0.9896[b]	0.7875E − 3									
4.0	0.7538	0.1415	0.2791E − 2	0.8221E − 6							
	0.7538	0.1415	0.2791E − 2	0.8221E − 6							
6.0	0.3752	0.3534	0.9179E − 1	0.6502E − 2	0.7354E − 4	0.1512E − 7					
	0.3752	0.3534	0.9179E − 1	0.6535E − 2	0.7354E − 4	0.1512E − 7					
8.0	0.1416	0.3064	0.2417	0.8371E − 1	0.1215E − 1	0.5866E − 3	0.5125E − 5	0.9000E − 9			
	0.1416	0.3064	0.2417	0.8371E − 1	0.1215E − 1	0.5866E − 3	0.5125E − 5	0.9000E − 9			
10.0	0.4659E − 1	0.1680	0.2493	0.1939	0.8327E − 1	0.1905E − 1	0.2056E − 2	0.8045E − 4	0.6124E − 6	0.1125E − 9	
	0.4659E − 1	0.1680	0.2493	0.1939	0.8327E − 1	0.1905E − 1	0.2056E − 2	0.8045E − 4	0.6124E − 6	0.1014E − 9	
12.0	0.1453E − 1	0.7404E − 1	0.1654	0.2110	0.1673	0.8416E − 1	0.2618E − 1	0.4699E − 2	0.4233E − 3	0.1492E − 4	0.1035E − 6
	0.1453E − 1	0.7404E − 1	0.1654	0.2110	0.1675	0.8412E − 1	0.2618E − 1	0.4699E − 2	0.4233E − 3	0.1456E − 4	0.1029E − 6
14.0	0.4499E − 2	0.2942E − 1	0.8760E − 1	0.1561	0.1842	0.1498	0.8472E − 1	0.3276E − 1	0.8297E − 2	0.1282E − 2	0.1023E − 3
	0.4499E − 2	0.2942E − 1	0.8760E − 1	0.1561	0.1842	0.1498	0.8472E − 1	0.3276E − 1	0.8297E − 2	0.1269E − 2	0.1013E − 3
16.0	0.1414E − 2	0.1119E − 1	0.4125E − 1	0.9370E − 1	0.1460	0.1644	0.1368	0.8453E − 1	0.3833E − 1	0.1247E − 1	0.2757E − 2
	0.1414E − 2	0.1119E − 1	0.4125E − 1	0.9370E − 1	0.1460	0.1644	0.1368	0.8453E − 1	0.3833E − 1	0.1240E − 1	0.2722E − 2
18.0	0.4572E − 3	0.4205E − 2	0.1829E − 1	0.4999E − 1	0.9588E − 1	0.1366	0.1491	0.1265	0.8363E − 1	0.4286E − 1	0.1684E − 1
	0.4572E − 3	0.4205E − 2	0.1829E − 1	0.4999E − 1	0.9588E − 1	0.1366	0.1491	0.1265	0.8363E − 1	0.4275E − 1	0.1658E − 1
20.0	0.1527E − 3	0.1588E − 2	0.7897E − 2	0.2497E − 1	0.5627E − 1	0.9596E − 1	0.1282	0.1368	0.1179	0.8291E − 1	0.4691E − 1
	0.1527E − 3	0.1588E − 2	0.7897E − 2	0.2497E − 1	0.5627E − 1	0.9596E − 1	0.1282	0.1368	0.1179	0.8216E − 1	0.4607E − 1

[a] Results of Lie-algebraic calculations with operators upto S_7 included

[b] Results of converged basis set calculations

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.

4 Concluding remarks

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 [16]. 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 [23] 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 [30]

$$U_c = \exp(S) \tag{4.1}$$

and decomposes the cluster operator into one, two, three, ..., N-body excitation operators. Generalizing to the open-shell systems, the CCM posits [29]

$$U = U_c U_v \tag{4.2}$$

where U_v 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 [29]. According to it, the cluster amplitudes corresponding to the fewer particle subsystem 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 applicability of the CCM for evaluating the ground state energy of the AHOs has been studied quite extensively over the past few years [33–38]. 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. We find a similar situation in the present time dependent context also. Second, Kaulfuss and Altenbokum [35] showed that the CCM wave functions in the boson representation are not always normalizable and 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 physicaly relevant quantities such as expectation values since U^+ can be replaced with U^{-1} and Hausdorff expansion 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 [36, 37]. 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 transition probabilities. While we found no evidence of this in our calculations, 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. Our numerical studies in Sect. 3 give support to this expectation. While the results presented in Sect. 3 are on one class of anharmonic systems, we stress that the formalism developed in Sect. 2 and the conclusions drawn here are more general and are valid for any anharmonic system, because, as we have shown in Sect. 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 approach receives contributions from *all* the basis functions in the Hilbert space because of its exponential structure. For example,

$$U_0|0\rangle = \exp[\sum_m S_{m0} a^{+m}|0\rangle$$

$$= \exp(S_{00})\{|0\rangle + S_{10}|1\rangle + (S_{20} + S_{10}^2/2!)|2\rangle + \ldots\}. \quad (4.3)$$

Even when S is approximated by a finite number of operators, the series in (4.3) 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. Second, for multidimensional systems, the size of the basis set required for C.I. based approaches increases exponentially with the number of degrees of freedom in the system. There has been considerable progress in recent years in propagating wave functions in time [1, 39] using discrete variable representation [40]. These methods primarily try to improve the efficiency of the matrix multiplication H with φ by exploiting the separability of some zero order hamiltonian such as the kinetic energy operator such that the computational resources scale linearly with dimension of the Hilbert space N. Thus, the exponential increase in the system requirement remains in all such approaches [39]. On the other hand, we expect the number of cluster

operators required to provide a numerically converged U to increase 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.

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 $L_0 = \{q^m p^n;\ 0 \leqslant m, n \leqslant \infty\}$ where q and p are the coordinate and momentum operators respectively. The decoupling procedure discussed in Sect. 2 is operative here also and the evolution operator can be written as, for example,

$$U = \exp\left[\sum_{m=1} S_{m0} q^m\right] \exp\left[\sum_{m=2} S_{m1} q^m p\right] \ldots \tag{4.4}$$

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 nonterminating series.

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