A General Algebraic Model for Molecular Vibrational Spectroscopy

A. Frank\textsuperscript{1,2}, R. Lemus\textsuperscript{1}, R. Bijker\textsuperscript{1}, F. Pérez-Bernal\textsuperscript{3} and J.M. Arias\textsuperscript{3}

\textsuperscript{1} Instituto de Ciencias Nucleares, UNAM
Apdo. Postal 70-543, Circuito Exterior, C.U.
04510 México, D.F., México.

\textsuperscript{2} Instituto de Física, Laboratorio de Cuernavaca, UNAM
Apdo. Postal 139-B, Cuernavaca, Morelos, México

\textsuperscript{3} Departamento de Física Atómica, Molecular y Nuclear
Facultad de Física, Universidad de Sevilla
Apdo. 1065, 41080 Sevilla, España

ABSTRACT

We introduce the Anharmonic Oscillator Symmetry Model to describe vibrational excitations in molecular systems exhibiting high degree of symmetry. A systematic procedure is proposed to establish the relation between the algebraic and configuration space formulations, leading to new interactions in the algebraic model. This approach incorporates the full power of group theoretical techniques and provides reliable spectroscopic predictions. We illustrate the method for the case of $D_{3h}$-triatomic molecules.
1. Introduction

Spectroscopic techniques represent one of the most important tools in modern chemical analysis.\(^1\) In particular, the molecular vibrational degrees of freedom are studied by means of Infrared and Raman spectroscopy.\(^2\) It is necessary, however, to rely on theoretical models in order to interpret the data, which in turn refines the models in a feedback cycle.

The study of molecular vibrational excitations is carried out by taking into account different degrees of approximations and theoretical assumptions. The simplest way to study the molecular energy spectra is by means of a Dunham expansion.\(^2\) This method, however, does not provide wave functions, and consequently does not allow the calculation of physical properties such as transition intensities. On the other hand there are \textit{ab initio} calculations, where an exact solution of the Schrödinger equation is attempted. In practice, the molecular Hamiltonian is usually parametrized as a function of internal coordinates and the potential modeled in terms of force field constants,\(^3\) which are determined either through calculations involving the molecular electronic states for several configurations\(^4\) or empirically, by the fitting of experimental data.\(^5\) While for diatomic and triatomic molecules very accurate information on force field constants is available,\(^6\) this is not the case for polyatomic molecules, due to the large size of their configuration spaces. It is thus important to develop alternative calculational methods in order to describe complex molecules for which \textit{ab initio} calculations are not feasible.

Algebraic models attempt to provide such alternative techniques. In 1981 an algebraic approach was proposed to describe the roto-vibrational structure of diatomic molecules,\(^7\) subsequently extended to linear tri- and four-atomic molecules\(^8\) and certain non-linear triatomic molecules.\(^9\) Although these results were encouraging, the model could not in practice be extended to polyatomic molecules, for which it is necessary to incorporate the underlying discrete symmetries. This difficulty can be surmounted by treating the vibrational degrees of freedom separately from the rotations. In 1984 Van Roosmalen
et al proposed a U(2)-based model to describe the stretching vibrational modes in ABA molecules,\textsuperscript{10} later extended to describe the stretching vibrations of polyatomic molecules such as octahedral and benzene like molecules.\textsuperscript{11} Recently the bending modes have also been incorporated to the framework, which was then applied to describe $C_{2v}$-triatomic molecules\textsuperscript{12} and the lower excitations of tetrahedral molecules,\textsuperscript{13} using a scheme which combines Lie-algebraic and point group methods. In a different approach, it has also been suggested to use a $U(k+1)$ model for the $k = 3n - 3$ rotational and vibrational degrees of freedom of a $n$-atomic molecule. This model has the advantage that it incorporates all rotations and vibrations and takes into account the relevant point group symmetry,\textsuperscript{14} but for larger molecules the number of possible interactions and the size of the Hamiltonian matrices increase very rapidly, making it impractical to apply.

The algebraic formulations have no doubt proved useful, but several problems remained, the most important of which is the absence of a clear connection to configuration space traditional methods, which in turn makes their significance difficult to gauge. A related problem is the lack of a systematic procedure to construct the physically meaningful interactions in the algebraic space. In this paper we address both these issues and introduce a general model for the analysis of molecular vibrational spectra, which we call the Anharmonic Oscillator Symmetry Model (AOSM). We shall show that it is possible to construct algebraic operators with a well defined physical interpretation and in particular the interactions which are of special relevance for the description of the degenerate modes present in systems exhibiting high degree of symmetry. These are derived in a procedure that takes full advantage of the discrete symmetry of the molecule and that provides all possible terms in a systematic fashion. As a bonus, a clear-cut connection is established between the algebraic scheme and the traditional analyses based on internal coordinates, which correspond to the harmonic limit of the model.

As a test for this approach we apply the AOSM to three $D_{3h}$-triatomic molecular systems, namely $Na_3^+$, Be$_3$ and H$_3^+$. We have chosen this set of molecules because they
cover a wide range of behaviors. Whereas Na3+ is very harmonic, H3+ displays a strongly anharmonic spectrum, while the Be3 cluster has an intermediate behavior. Since these small molecules can be very well described by means of *ab initio* calculations,\textsuperscript{15,16} we again emphasize the aim of this work. We shall establish an exact correspondence between configuration space and algebraic interactions in the harmonic limit of the U(2) algebra. This general procedure not only allows to derive the interactions in the AOSM from interactions in configuration space, but can also be applied to cases for which no configuration space interactions are available. The $D_{3h}$-triatomic molecules constitute the simplest systems where degenerate modes appear and where the new interactions in the model become significant. The application of these techniques to more complex systems, such as tetrahedral molecules, is presented elsewhere.\textsuperscript{17)}

In the next section the structure of the model is presented. Section 3 is devoted to the construction of the symmetry adapted normal basis, which is the most appropriate one to carry out the diagonalizations. In Section 4 we propose a new set of interactions which have physical interest and suggest the need to construct operators associated to the $E$ mode. In Section 5 we describe the general procedure to derive the algebraic interactions from those appearing in configuration space and in Section 6 we introduce the AOSM in order to derive all algebraic interactions from symmetry considerations. In Section 7 we apply the model to H3+, Be3 and Na3+, while in Section 8 we present our conclusions and discuss some future developments of the model.
2. Algebraic Model

The model exploits the isomorphism of the $U(2)$ Lie algebra and the one dimensional Morse oscillator

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D(e^{-\frac{2x}{\hbar}} - 2e^{-\frac{x}{\hbar}}),$$  \hspace{1cm} (2.1)$$

whose eigenstates $\mathcal{E}$ can be associated with $U(2) \supset SO(2)$ states.\textsuperscript{18}) In order to see how this isomorphism comes about, consider the radial equation

$$\frac{1}{2} \left( -\frac{1}{r} \frac{d}{dr} r \frac{d}{dr} + \frac{m^2}{r^2} + r^2 \right) \phi(r) = (N + 1)\phi(r),$$  \hspace{1cm} (2.2)$$

which corresponds to a two-dimensional harmonic oscillator (in units where $\hbar = \mu = e = 1$) associated to a $U(2)$ symmetry algebra.\textsuperscript{19}) By carrying out the transformation

$$r^2 = (N + 1)e^{-\rho},$$

equation (2.2) transforms into

$$\left[ -\frac{d^2}{d\rho^2} + \left( \frac{N + 1}{2} \right)^2 (e^{-2\rho} - 2e^{-\rho}) \right] \phi(\rho) = -m^2 \phi(\rho),$$  \hspace{1cm} (2.3)$$

which can be identified with (2.1) after defining $x = \rho d$ and multiplying by $\hbar^2/2\mu d^2$, provided that

$$D = \frac{\hbar^2}{8\mu d^2}(N + 1)^2,$$
$$\mathcal{E} = -\frac{\hbar^2}{2\mu d^2} m^2.$$  \hspace{1cm} (2.4a, 2.4b)$$

In the framework of the $U(2)$ algebra, the operator $\hat{N}$ corresponds to the total number of bosons and is fixed by the potential shape according to (2.4), while $m$, the eigenvalue of the $SO(2)$ generator $J_z$, takes the values $m = \pm N/2, \pm (N - 2)/2, \ldots$. The Morse spectrum is reproduced twice and consequently for these applications the $m$-values must
be restricted to be positive. In terms of the $U(2)$ algebra, it is clear from (2.3-4) that the Morse Hamiltonian has the algebraic realization

$$\hat{H} = -\frac{\hbar^2}{2\mu d^2} \hat{J}_z^2 = -A\hat{j}_z^2 .$$

(2.5)

In addition, the $U(2)$ algebra includes the raising and lowering operators $\hat{J}_+$, $\hat{J}_-$, which connect different energy states in (2.3), while the angular momentum operator is given by $\hat{j}_z^2 = \frac{1}{4}\hat{N}(\hat{N} + 2)$, as will be shown below.

The Morse Hamiltonian (2.5) can be rewritten in the more convenient form

$$\hat{H} = A\hat{H}^M = \frac{A}{2}[(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+) - \hat{N}] ,$$

(2.6)

where we have used the relation $\hat{j}_z^2 = \hat{j}_z^2 - \frac{1}{2}(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+)$ and added the constant term $\frac{A\hat{N}^2}{4}$ in order to place the ground state at zero energy. The eigenfunctions of the Hamiltonian (2.7) are associated to the $U(2) \supset O(2)$ chain, and are given by

$$U(2) \supset SO(2) \downarrow \downarrow \downarrow ||[N], v >$$

with

$$||[N], v > = \sqrt{\frac{(N - v)!}{N!v!}} (J_+)^v||[N], 0 >$$

(2.7)

where $N$ is the total number of bosons fixed by the potential shape (Eq. (2.4a)) and $v$ corresponds to the number of quanta in the oscillator. Both, $N$ and $v$, are related with the usual labels $j$ and $m$ of the $U(2)$ and $SO(2)$ groups, by means of

$$N = 2j$$

$$v = j - m .$$

(2.8)

The parameters $N$ and $A$ appearing in (2.6) are related to the usual harmonic and anharmonic constants $\omega_e$ and $x_e \omega_e$ used in spectroscopy. This is seen by substituting the
operator $J_z$ in (2.5) by its eigenvalue. In terms of $v$, the corresponding energy expression takes the form

$$E_M = -\frac{A}{2}(N + 1/2) + A(N + 1)(v + 1/2) - A(v + 1/2)^2 \ ,$$

from which we immediately obtain

$$\omega_e = A(N + 1) \ ,$$

$$x_e\omega_e = A \ .$$

Thus, in a diatomic molecule the parameters $A$ and $N$ can be determined by the spectroscopic constants $\omega_e$ and $x_e\omega_e$.

We now consider a particular molecular system. We start by assigning a $U^i(2)$ algebra to each relevant interatomic interaction.\(^{13}\) In figure 1 we show the $U^i(2)$ assignment for $D_{3h}$-triatomic molecules. All relevant operators in the model are then expressed in terms of the generators of the molecular dynamical group, which is given by the product

$$U^1(2) \otimes U^2(2) \otimes U^3(2) \ .$$

A simple realization for these generators can be given in terms of the number operator $\hat{N}_i$ and the operators $\hat{J}_{\mu,i}$

$$\{\hat{N}_i, \hat{J}_{x,i}, \hat{J}_{y,i}, \hat{J}_{z,i}\}, \ i = 1, 2, 3$$

with

$$\hat{N}_i = s_i^\dagger s_i + t_i^\dagger t_i \quad (2.12a)$$

$$\hat{J}_{x,i} = \frac{1}{2}(t_i^\dagger s_i + s_i^\dagger t_i), \ \hat{J}_{y,i} = \frac{i}{2}(t_i^\dagger s_i - s_i^\dagger t_i), \ \hat{J}_{z,i} = \frac{1}{2}(s_i^\dagger s_i - t_i^\dagger t_i) \ ,$$

where $s_i^\dagger(s_i)$ and $t_i^\dagger(t_i)$ are bosonic operators satisfying the usual commutation relations

$$[s_i, s_j^\dagger] = [t_i, t_j^\dagger] = \delta_{ij} \ .$$
All other commutators vanish. The operators (2.12b) satisfy the usual angular momentum commutation relations. Computing $\hat{J}^2_i = J_{x_i}^2 + J_{y_i}^2 + J_{z_i}^2$, we find

$$\hat{J}^2_i = \frac{\hat{N}_i}{2} \left( \frac{\hat{N}_i}{2} + 1 \right), \quad (2.13a)$$

from which the identification

$$j_i = \frac{N_i}{2}, \quad (2.13b)$$

is readily made. One can show directly from (2.12) or from (2.13a) that $[\hat{J}_{i,j}, \hat{N}_i] = 0$. The set (2.12b) thus defines the $SU_i(2)$ subalgebra of $U_i(2)$. Since $\hat{N}_i = N_i$ will remain fixed in our applications, we shall sometimes refer to $SU_i(2)$ instead of $U_i(2)$. The specific boson realization (2.12) was given for reasons of clarity, but is not necessary for the subsequent developments of the model.

Formally, while the vibrational symmetry group of the $X_3$ molecules is $D_{3h}$, in practice it can be reduced to $D_3$ due to the in-plane restriction. Since we are assigning a number to each bond it is more convenient to work with the symmetric group $S_3$, which is isomorphic to $D_3$ through the generator identification

$$C_3 \leftrightarrow (123),$$
$$C_{\alpha_v} \leftrightarrow (23),$$

as indicated in Fig. 1. The Hamiltonian of the system is then expanded in terms of the dynamical group generators (2.12), provided that we impose its invariance with respect to the symmetry group $S_3$. In order to explain the main features of the algebraic model we start by considering a simple form for the Hamiltonian, restricted to two body interactions which preserve the total number of quanta $V = \sum v_i$, where each $v_i$ is defined as in (2.8),

$$\hat{H} = A \sum_{i=1}^{3} \hat{H}_i^M + B \sum_{i,j=1 \atop i \neq j}^{3} \hat{H}_{ij} + \frac{\lambda}{2} \sum_{i,j=1 \atop i \neq j}^{3} \hat{V}_{ij}, \quad (2.14)$$
where the operators $\hat{H}_i^M$, $\hat{H}_{ij}$ and $\hat{V}_{ij}$ are defined as

$$\hat{H}_i^M = \frac{1}{2}(\hat{J}_{+i}\hat{J}_{-i} + \hat{J}_{-i}\hat{J}_{+i}) - \frac{\hat{N}_i}{2}, \quad (2.15a)$$

$$\hat{H}_{ij} = 2\hat{J}_{0i}\hat{J}_{0j} - \frac{\hat{N}_i\hat{N}_j}{2}, \quad (2.15b)$$

$$\hat{V}_{ij} = (\hat{J}_{+i}\hat{J}_{-j} + \hat{J}_{-i}\hat{J}_{+j}), \quad (2.15c)$$

The first term in (2.14) corresponds to three equivalent Morse oscillators (2.6), while the two terms $\hat{H}_{ij}$ and $\hat{V}_{ij}$ correspond to interactions diagonal in the chains associated to the couplings

$$SU^{(i)}(2) \otimes SU^{(j)}(2) \supset SO^{(i)}(2) \otimes SO^{(j)}(2) \supset SO^{(ij)}(2), \quad (2.16a)$$

$$SU^{(i)}(2) \otimes SU^{(j)}(2) \supset SU^{(ij)}(2) \supset SO^{ij}(2), \quad (2.16b)$$

respectively. The notation $SU^{(ij)}(2)$ indicates the usual angular momentum coupling of the $SU^{(i)}(2)$ and $SU^{(j)}(2)$ states.

The basis arising from three couplings of the form (2.16a) is referred to as the local basis, since the Morse oscillators are diagonal when the three $SO^i(2)$ algebras are well defined.\textsuperscript{10,19} It should be noted that for most calculations, higher order terms are required in the Hamiltonian (2.14) in order to attain higher accuracy, as we shall see in the following sections. The physical interpretation of these interactions will also be explained.

Once we have established the form of the Hamiltonian, we need a basis to carry out its diagonalization. Since the Hamiltonian is invariant under the symmetry group $S_3$, its eigenfunctions span irreducible representations (irreps) of this group for any given basis. It is convenient, however, to define a physical basis in order to classify the states with the usual normal mode labels, as well as to simplify the calculations.
3. Symmetry Adapted Normal Basis

The simplest basis to diagonalize the Hamiltonian (2.14) is the one associated to the local mode chain\(^{19}\)

\[
U^{(1)}(2) \otimes U^{(2)}(2) \otimes U^{(3)}(2) \supset SO^{(1)}(2) \otimes SO^{(2)}(2) \otimes SO^{(3)}(2) \supset SO(2)
\]

\[
|N_1|, |N_2|, |N_3|; v_1, v_2, v_3; V > ,
\]

where below each group we have indicated the eigenvalues that label their irreps. Explicitly this basis is given by,

\[
|[N_1], [N_2], [N_3]; v_1v_2v_3 > = |[N_1]; v_1 > |[N_2]; v_2 > |[N_3]; v_3 >
\]

where \([N_i]; v_i\) are given by (2.7). The index \(v_i\) corresponds to the number of quanta in the \(i\)-th oscillator, which is related to the eigenvalues \(j_i\) and \(m_i\) of the \(\hat{J}^2\) and \(\hat{J}_{z,i}\) operators by means of expressions (2.8) and (2.13)

\[
v_i = j_i - m_i .
\]

Since

\[
j_i = \frac{N_i}{2} , \quad m_i \geq 0 ,
\]

we find

\[
v_i = 0, 1, 2, \ldots, [N_i/2] .
\]

where \([x]\) indicates the integer part of \(x\). As mentioned above, \(V\) corresponds to the total number of quanta

\[
V = \sum_{i=1}^{3} v_i ,
\]

which is conserved by the interactions in (2.14)
The contributions to the Hamiltonian (2.14) involving $SO(2)$ operators are diagonal in the basis (3.1)

\[
< [N_1], [N_2], [N_3]; v_1, v_2, v_3; V|\hat{H}_i^M|[N_1], [N_2], [N_3]; v_1, v_2, v_3; V > = -v_i^2 + N_i v_i \ , (3.6)
\]

\[
< [N_1], [N_2], [N_3]; v_1, v_2, v_3; V|\hat{H}_{ij}|[N_1], [N_2], [N_3]; v_1, v_2, v_3; V > = 2v_i v_j - (v_i N_j + v_j N_i) \ , \quad (3.7)
\]

while the $\hat{V}_{ij}$ operator has only non-diagonal matrix elements, since it involves the raising and lowering operators in the $i, j$ indices,

\[
< [N_1], [N_2], [N_3]; v_1', v_2', v_3'; V|\hat{V}_{ij}|[N_1], [N_2], [N_3]; v_1, v_2, v_3; V > = \sqrt{v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)} \delta_{v_i, v_i+1} \delta_{v_j, v_j-1} + \sqrt{v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)} \delta_{v_i', v_i-1} \delta_{v_j', v_j+1} \ , \quad (3.8)
\]

with $i, j = 1, 2, 3$ and $i < j$. Note that because of the symmetry of the $D_3$ system the same number of bosons $N_i = N$ (i.e. the same potential depth) is assigned to all three bonds.

In the next Section the physical meaning of these interactions will become clear. These analytical results for the matrix elements and analogous ones for higher order interactions constitute one of the main advantages of the model. We point out, however, that although the local basis is convenient from a numerical point of view, it does not span the irreps of $S_3$. A better way to carry out the diagonalization of (2.14) is to symmetrize the local basis (3.1), for which we can either symmetry-project the wave functions arising from the local basis once the Hamiltonian has been diagonalized, or generate the symmetry adapted one-phonon states and then construct the higher-phonon states by means of coupling coefficients.\(^{13}\) For our purposes it is better to follow the second route, since in this way the wave functions explicitly carry the normal labels from the outset. In the case where spurious modes are present, the building-up procedure is essential, since in this way the unphysical modes can be exactly eliminated from the space.\(^{13}\)
In order to construct the normal basis we start by establishing explicit forms for the irreps of the group $S_3$. For practical reasons it is convenient to work with real representations, so we have chosen the cartesian harmonics as a basis for the $E$ representation. In Table I we show the character table of the $S_3$ group, including at the right the basis functions spanning the irreducible representations. In Table II we indicate the explicit irrep $E$ carried by these functions in the reference frame of Figure 1.

We now consider the one-phonon local functions. In this case the basis (3.1) has the form

\begin{align}
|1 > & \equiv |[N], [N], [N]; 100; 1 > , \\
|2 > & \equiv |[N], [N], [N]; 010; 1 > , \\
|3 > & \equiv |[N], [N], [N]; 001; 1 > , \quad (3.12)
\end{align}

which can be readily projected to the normalized states

\begin{align}
^1\psi^{A_1} &= \frac{1}{\sqrt{3}} \left\{ |1 > + |2 > + |3 > \right\}, \\
^1\psi^E_1 &= \frac{1}{\sqrt{6}} \left\{ 2|1 > - |2 > - |3 > \right\}, \\
^1\psi^E_2 &= \frac{1}{\sqrt{2}} \left\{ |2 > - |3 > \right\}, \quad (3.13)
\end{align}

where we have used the notation $V^\Gamma_\gamma$ for the wave functions. For higher phonon number the states are obtained through the coupling\textsuperscript{13)}

\[ V_1 + V_2 \Psi^\Gamma_\gamma = \sum_{\gamma_1, \gamma_2} C(\Gamma_1 \Gamma_2 \Gamma; \gamma_1 \gamma_2 \gamma) \, V_1 \Psi_{\gamma_1} \, V_2 \Psi_{\gamma_2} , \quad (3.14) \]

where the coupled wave functions now correspond to a total number of phonons $V = V_1 + V_2$. The coupling (Clebsch-Gordan) coefficients $C(\;)$ can be found in tables\textsuperscript{20)} or, in order to avoid phase inconsistencies, computed in a straightforward way using the explicit irrep given in Table II.\textsuperscript{21)} In Table III we present the Clebsch-Gordan coefficients derived in this fashion.
Using (3.14) repeatedly leads to a building-up procedure to derive the symmetry adapted basis for higher-phonon numbers. To achieve this task, however, we must obtain the decomposition of the products \((A_1)^{v_{A_1}} (E)^{v_E}\), where \(v_{A_1}, v_E\) correspond to the number of phonons in the normal modes. In Table IV we indicate, as an example, the reductions for two and three quanta. The procedure to obtain these reductions is a standard one, explained in many group theory textbooks.\(^{21}\) One should bear in mind, however, that the boson nature of the vibrations implies that only symmetrized products are allowed for phonons in the same mode. For example, for two quanta in the \(E\) mode we have in general the following reduction in terms of the symmetric \([\ ]\) and antisymmetric \(\{\}\) contributions\(^{21}\)

\[
E \otimes E = [E \otimes E] \oplus \{E \otimes E\} ,
\]

where

\[
[E \otimes E] = A_1 \oplus E ; \quad \{E \otimes E\} = A_2 .
\]

Since the two phonon state (3.14) associated to the product \(\{E \otimes E\}\) vanishes automatically, we are left only with the symmetrized product \([E \otimes E]\).

The general procedure is now clear. Once the form of the Hamiltonian has been determined by symmetry considerations, we proceed to construct the symmetry adapted basis by projecting the one-phonon local functions. The higher-phonon functions are then generated from the one-phonon symmetrized states by means of the coupling (3.14). Finally, we carry out the diagonalization in the symmetrized basis, where full advantage can be taken of group-theoretical properties. In particular, the Hamiltonian matrix separates into blocks corresponding to the irreps of the symmetry group \(S_3\). For example, from Table IV we see that in the three phonon manifold the number of functions is 10, which reduce to three blocks of dimensions \(3 \times 3, 1 \times 1\) and \(3 \times 3\), corresponding to the irreps \(A_1, A_2\) and \(E\), respectively. The simplification becomes more significant as the complexity of the molecular system and/or the phonon number increase.\(^{13}\)
4. Analysis of Interactions

We now proceed to analyze the interactions involved in the Hamiltonian (2.14). In order to do so it is convenient to recall the standard labeling of states as well as the vibrational Dunham expansion for $D_{3h}$-triatomic molecules.\(^2\)

As is well known, this type of molecules exhibit three vibrational degrees of freedom, which give rise to two normal modes associated to $A_1$ and $E$ symmetries. The normal states are then specified by the number of quanta in each mode $|v_{A_1}, v_E\rangle$. In addition, the double degenerate $E$ mode carries an intrinsic angular momentum $l$, whose values depend on $v_E$ and are given by\(^2\)

$$l = v_E, \; v_E - 2, \ldots, 1 \; \text{ or } \; 0.$$  \hspace{1cm} (4.1)

The states are then specified by the quantum numbers $v_{A_1}, v_E$ and $l$ with the notation

$$|v_{A_1}, v_E^l\rangle.$$  \hspace{1cm} (4.2)

The simplest way to reproduce the general features of the spectrum is by means of a Dunham expansion, which up to quadratic terms takes the form\(^2\)

$$E_v(v_{A_1}, v_E, l) = E_0 + \omega_e^{A_1}(v_{A_1} + 1/2) + \omega_e^{E}(v_E + 1)$$

$$- x_e\omega_e^{A_1}(v_{A_1} + 1/2)^2 - x_e\omega_e^{E}(v_E + 1)^2$$

$$+ x_{12}(v_A + 1/2)(v_E + 1) + g_{22}l^2,$$  \hspace{1cm} (4.3)

The first two terms in the sum correspond to the harmonic contributions to the energy, while the next three terms, $(v_A + 1/2)^2$, $(v_E + 1)^2$ and $(v_{A_1} + 1/2)(v_E + 1)$, represent the first anharmonic corrections. The last term is the intrinsic (or vibrational) angular momentum and gives rise to the correct ordering for states with the same value of the quantum numbers $v_{A_1}$ and $v_E$. In addition, each wave function $|v_{A_1}, v_E^l\rangle$ carries a definite
symmetry, which is closely related to the $l$ quantum number. For $l = 0$ the states are totally symmetric and labeled as $a_1$ (we use lower case letters to denote the symmetry). For $l = 3k$, $k = 1, 2, 3, \ldots$, two levels corresponding to $a_1$ and $a_2$ symmetries appear, while for $l = 3k + 1$ or $l = 3k + 2$, $k = 0, 1, 2, \ldots$, the states exhibit $e$ symmetry. Note that for $l \neq 0$ there are two components $\pm l$, although this is not explicit in the notation.\(^2\)

We remark that the expansion (4.3) does not remove the degeneracy of the levels $a_1$ and $a_2$ associated to the $l = 3k$ states. The same is true for any order in the Dunham expansion. Experimentally this degeneracy is not present, but this cannot be taken into account by such simple parametrizations.

Let us now analyze the interactions involved in (2.14). If we compute the matrix elements of the operators $\sum \hat{H}_{ij}$ and $\sum \hat{V}_{ij}$ in the one-phonon manifold, we obtain

\[
<^1 \psi^{A_1} | \sum \hat{H}_{ij}|^1 \psi^{A_1} > = -2N , \quad (4.4a)
\]

\[
<^1 \psi^{A_1} | \sum \hat{V}_{ij}|^1 \psi^{A_1} > = 2N , \quad (4.4b)
\]

\[
<^1 \psi^{E_\gamma} | \sum \hat{H}_{ij}|^1 \psi^{E_\gamma} > = -2N , \quad \gamma = 1, 2 . \quad (4.5a)
\]

\[
<^1 \psi^{E_\gamma} | \sum \hat{V}_{ij}|^1 \psi^{E_\gamma} > = -N , \quad \gamma = 1, 2 . \quad (4.5b)
\]

From these results we conclude that the operator

\[
\hat{H}_E \equiv -\frac{1}{3} \{ \sum V_{ij} + \sum H_{ij} \} \quad (4.6)
\]

does not contribute to the energy of the $A_1$ mode. The $-1/3$ factor was added for later convenience. In Figure 2 we show the spectrum generated by (4.6) for the two and three phonon manifolds, as a function of $N$. Note that for large $N$ the operator (4.6) behaves as $\hat{n}_E$, the number of phonons in the $E$ mode, a result we shall explain in Section 5.

The previous analysis leads to the question of whether it is possible to construct from (2.15) an operator affecting only the $A_1$ mode. This is indeed possible and through projection we find

\[
\hat{H}_{A_1} \equiv \frac{1}{3} \{ \sum \hat{V}_{ij} - \frac{1}{2} \sum \hat{H}_{ij} \} , \quad (4.7)
\]
which satisfies
\[
<^1 \psi_i^E | \hat{H}_{A_1} | ^1 \psi_i^E > = 0 , \quad \gamma = 1, 2 ,
\] (4.8)
as required. We show in Figure 3 the spectrum generated by (4.7) as a function of \( N \). For large \( N \) the operator (4.7) behaves as \( \hat{n}_{A_1} \), the number of phonons in the \( A_1 \) mode (see Section 5).

We have thus constructed operators that selectively affect to the \( A_1 \) and \( E \) modes. The Hamiltonian (2.4), however, includes three independent operators. A third operator can be easily derived:
\[
\hat{V} \equiv \sum_{i=1}^{3} \hat{H}_i^M + \frac{(N-1)}{2N} \sum_{i,j=1}^{3} \hat{H}_{ij} ,
\] (4.9)
which is diagonal in the local basis (3.1) and satisfies
\[
<^1 \psi_i^{A_1} | \hat{V} | ^1 \psi_i^{A_1} > = 0 , \quad \gamma = 1, 2 ,
\] (4.10a)
\[
<^1 \psi_i^{E} | \hat{V} | ^1 \psi_i^{E} > = 0 , \quad \gamma = 1, 2 .
\] (4.10b)
In Figure 4 we schematically show the effect of \( V \) as a function of \( N \) in the two and three-phonon manifolds. Note that this operator is diagonal in the local basis and vanishes in the large \( N \) limit.

The method followed in this section is general and indicates a procedure to define operators with definite actions over the physical space. Additionally, the use of these symmetry adapted operators significantly improves the convergence of the mean square search of parameters in the diagonalization of the Hamiltonian.

Although the operators (4.6), (4.7) and (4.9) induce the characteristics of the spectrum generated by the harmonic and anharmonic contributions in (4.3), they cannot reproduce the effect of the \( l^2 \) term. This term orders, for a positive (negative) value of \( g_{22} \), the vibrational levels in each phonon multiplet \( (v_{A_1}, v_E') \) according to increasing (decreasing) value of \( l \). Figures 2-4 indicate that the characteristic pattern of the \( D_{3h} \) vibrational spectrum cannot be reproduced by the simple Hamiltonian
\[
\hat{H} = \alpha \hat{H}_{A_1} + \beta \hat{H}_E + \gamma \hat{V} .
\] (4.11)
This analysis, however, does show that the simple algebraic Hamiltonian (2.14) can be interpreted in a physically meaningful way by concentrating on the symmetry properties of the interactions, as expressed in (4.11). In the next section we present a systematic procedure to derive the full set of interactions in the algebraic framework, starting from those present in configuration space.

5. Algebraic Interactions and Configuration Space Operators

In order to establish the algebraic representation of configuration-space operators, we start by analyzing the harmonic limit of the angular momentum operators

\[
[\hat{J}_0, \hat{J}_\pm] = \pm \hat{J}_\pm, \quad (5.1a)
\]
\[
[\hat{J}_+, \hat{J}_-] = 2\hat{J}_0. \quad (5.1b)
\]

The action of the \(\hat{J}_\pm\) on the Morse states \(|[N], v>\) is given by

\[
\hat{J}_+[N], v > = \sqrt{v(N - v + 1)} \, |[N], v - 1>, \quad (5.2a)
\]
\[
\hat{J}_-[N], v > = \sqrt{(N - v)(v + 1)}|[N], v + 1>, \quad (5.2b)
\]

where \(N\) and \(v\) were defined in (3.2) and (3.3). Defining the change of scale transformation

\[
\bar{b} \equiv \frac{\hat{J}_+}{\sqrt{N}}, \quad \bar{b}^\dagger \equiv \frac{\hat{J}_-}{\sqrt{N}}, \quad (5.3)
\]

it is clear that

\[
\lim_{N \to \infty} \bar{b} \, |[N]v > = \sqrt{v}|[N], v - 1>, \quad (5.4a)
\]
\[
\lim_{N \to \infty} \bar{b}^\dagger |[N]v > = \sqrt{v + 1}|[N], v + 1>. \quad (5.4b)
\]

which correspond to the harmonic limit of the model, as expected from the role of \(N\) in Eq. (2.4), i.e., for infinite potential depth the Morse potential cannot be distinguished
from an harmonic potential. Using the definitions (3.2), (3.3) and (5.3), we can rewrite the commutation relation (5.1a) in the new form:

\[
[\hat{b}, \hat{b}^\dagger] = 1 - \frac{2\hat{v}}{N} ,
\]

(5.5a)

where

\[
\hat{v} = \frac{\hat{N}}{2} - \hat{J}_0
\]

(5.5b)
is the Morse phonon operator corresponding to the definition (3.2). The limit \(N \to \infty\) leads to the contraction of the \(SU(2)\) algebra to the Weyl algebra generated by \(b, b^\dagger\) and 1, with the usual boson commutation relation \([b, b^\dagger] = 1\). Relations (5.3-5.5) indicate the procedure to arrive at the harmonic limit of the model. Each \(\hat{J}_{+i}, \hat{J}_{-i}\) should be renormalized by dividing by \(\sqrt{N_i}\) and then take the limit \(N_i \to \infty\).

As an example of this procedure we take the harmonic limit of the Morse Hamiltonian (2.7)

\[
\lim_{N \to \infty} \frac{1}{N} \hat{H}^M = \lim_{N \to \infty} \frac{1}{N} \left[ \frac{1}{2} \left( \hat{J}_- \hat{J}_+ + \hat{J}_+ \hat{J}_- \right) - \frac{\hat{N}}{2} \right]
\]

\[
= \frac{1}{2} (b^\dagger b + bb^\dagger) - \frac{1}{2}
\]

\[
= b^\dagger b ,
\]

(5.6)

which has eigenvalues \(n_b\), in agreement with the harmonic limit of Eq. (2.9). Applying the same procedure to the symmetry projected interactions of Eq. (4.11) we find

\[
\lim_{N \to \infty} \frac{1}{N} \hat{H}_{A_1} = \hat{n}_{A_1} ,
\]

\[
\lim_{N \to \infty} \frac{1}{N} \hat{H}_E = \hat{n}_E ,
\]

\[
\lim_{N \to \infty} \frac{1}{N} \hat{\mathcal{V}} = 0 ,
\]

(5.7)

where \(\hat{n}_{A_1}\) and \(\hat{n}_E\) are the operators corresponding to the number of phonons in the \(A_1\) and the \(E\) modes, respectively, as can be readily shown using the technique discussed below.
We can now interpret Eq. (5.3) in the opposite sense, i.e. as a way to construct the anharmonic representation of harmonic operators. Any given function of $b, b^\dagger$ can be mapped into the same function of $\hat{J}_+, \hat{J}_-$ through the correspondence
\[
b \to \frac{\hat{J}_+}{\sqrt{N}}, \quad b^\dagger \to \frac{\hat{J}_-}{\sqrt{N}}. \tag{5.8}
\]
As an example, we consider again the one-dimensional harmonic oscillator
\[
\hat{H} = \frac{1}{2}(b^\dagger b + bb^\dagger), \tag{5.9}
\]
with eigenvalues $E = n_b + 1/2$, and follow the reverse order in (5.6). To obtain its anharmonic representation we carry out the correspondence (5.8) to get
\[
\hat{H} \to \frac{1}{2N}(\hat{J}_-\hat{J}_+ + \hat{J}_+\hat{J}_-) \\
= \frac{1}{N}(\hat{J}^2 - \hat{J}_0^2) = \hat{v} + 1/2 - \hat{v}^2/N, \tag{5.10}
\]
which is the algebraic realization of the Morse oscillator, as shown in Section 2.

The general procedure to derive the algebraic realization of a given configuration-space operator is thus the following. We first write down the operator in terms of normal coordinates and momenta $\{q,p\}_\Gamma^\gamma$, and express it in terms of the harmonic bosons
\[
b_{\Gamma}^\gamma \dagger = \frac{1}{\sqrt{2}}(q - ip)_\Gamma^\gamma, \\
b_{\Gamma}^\gamma = \frac{1}{\sqrt{2}}(q + ip)_\Gamma^\gamma, \tag{5.11}
\]
where $\Gamma$ denotes the irrep spanned by the normal coordinate and $\gamma$ is its row. In the next step we write down the normal operators $\{b_{\Gamma}^\gamma, b^\dagger_{\Gamma}^\gamma\}$ in terms of local ones $\{b_i^\dagger, b_i\}$. The explicit relations are of the general form
\[
b_{\Gamma}^\gamma \dagger = \sum_i \alpha_{\Gamma,i}^\gamma b_i^\dagger \\
b_{\Gamma}^\gamma = \sum_i \alpha_{\Gamma,i}^\gamma b_i, \tag{5.12}
\]
where the set \( \{ \alpha_{\gamma,i}^\Gamma \} \) can be obtained by projecting the local operators \( \{ b_i^\dagger \} \) on the irrep spanned by the normal coordinates \( \{ q, p \}^\Gamma_{\gamma} \). Finally, we substitute (5.12) in the expression of the interaction given in terms of the normal operators (5.11) and carry out the correspondence (5.8). As an example of this procedure we derive the algebraic form of the \( \hat{l}^2 \) interaction in (4.3).

The representation of the operator \( \hat{l} \) in terms of normal coordinates \( q^E_{1}, q^E_{2} \), which span the irrep \( E \), is given by

\[
\hat{l} = -i \left( q^E_1 \frac{\partial}{\partial q^E_2} - q^E_2 \frac{\partial}{\partial q^E_1} \right). \tag{5.13}
\]

Introducing the operators (5.11), this expression transforms into

\[
\hat{l} = -i(b^E_{2 \dagger} b^E_{1} - b^E_{1 \dagger} b^E_{2}) . \tag{5.14}
\]

We now write the normal operators \( \{ b^E_{1 \dagger}, b^E_{2 \dagger} \} \) in terms of the local ones \( \{ b_i^\dagger \} \). This can be done using the projected functions (3.13)

\[
b^E_{1 \dagger} = \frac{1}{\sqrt{6}}(2b_1^\dagger - b_2^\dagger - b_3^\dagger) ,
\]

\[
b^E_{2 \dagger} = \frac{1}{\sqrt{2}}(b_2^\dagger - b_3^\dagger) , \tag{5.15}
\]

and equivalent expressions for the annihilation operators. Finally, we substitute (5.15) into (5.14) to obtain

\[
\hat{l}_{A_2} = \frac{i}{\sqrt{3}} \{ b_1^\dagger(b_2 - b_3) + b_2^\dagger(b_3 - b_1) + b_3^\dagger(b_1 - b_2) \} , \tag{5.16}
\]

where we have explicitly indicated the irrep carried by the \( \hat{l} \) operator. The fact that it corresponds to an \( A_2 \) symmetry can be deduced either by analyzing the transformation of \( \hat{l} \) under the \( S_3 \) group or by identifying the Clebsch-Gordan coefficients \( C(EEA_2;\gamma_1\gamma_21) \) in (5.14). The corresponding realization in the model is then obtained by applying the correspondence (5.8)

\[
\hat{l}_{A_2} = \frac{i}{N\sqrt{3}} \{ \hat{J}_{-1}(\hat{J}_{+2} - \hat{J}_{+3}) + \hat{J}_{-2}(\hat{J}_{+3} - \hat{J}_{+1}) + \hat{J}_{-3}(\hat{J}_{+1} - \hat{J}_{+2}) \} . \tag{5.17}
\]
In turn, the $\hat{l}_{A_2}^2$ operator is obtained by squaring (5.17). The same kind of analysis can be applied to arbitrary configuration space interactions.\textsuperscript{22})

We have presented in this section a general method to derive the realization of operators in the algebraic model, starting from their representation in configuration space. This procedure considerably increases the power of the algebraic approach, since it can be used to incorporate into the model the fundamental interactions known from the configuration space methods. Note that this procedure allows, in principle, to establish the relation between the algebraic parameters and the force field strengths obtained from \textit{ab initio} calculations. It is also possible, however, to apply the model in a purely algebraic fashion and still deduce the fundamental interactions, as we explain in the next Section.

6. The Anharmonic Oscillator Symmetry Model

In this Section we present a general framework to construct all interactions in the algebraic model in a systematic way. We shall henceforth refer to this procedure, together with the methods introduced in the previous sections, as the Anharmonic Oscillator Symmetry Model (AOSM).

We start by introducing a set of generators with well-defined tensorial properties under the point group

$$\hat{J}_{\mu,\gamma} = \sum_i \alpha_{\gamma,i} \hat{J}_{\mu,i} \ ,$$

where $\mu = +, -, 0$. For the case of $D_{3h}$ molecules the expansion coefficients are the same as those in Eq. (5.12). We then construct from these symmetry projected generators a set of interactions that are scalars under the point group, such as

$$T_{A_1}^\pm (\Gamma) = \frac{1}{2} \sum_\gamma \left( \hat{J}_{-\gamma,\gamma} \hat{J}_{+\gamma,\gamma} + \hat{J}_{+\gamma,\gamma} \hat{J}_{-\gamma,\gamma} \right) \ , \quad (6.2a)$$

and
\[ T_6^{A_1} = (\Gamma) \sum_{\gamma} \hat{J}_{\gamma}^\Gamma \hat{J}_{\gamma}^\Gamma. \]  

(6.2b)

Higher order tensors can be systematically constructed by means of (6.1) and the Clebsch-Gordan coefficients for the point group.

For triatomic \( D_{3h} \)-molecules \( \Gamma = A_1, E \), the relevant symmetry projected generators are

\[ \hat{J}_{\mu,1}^A = \frac{1}{\sqrt{3}} \left( \hat{J}_{\mu,1} + \hat{J}_{\mu,2} + \hat{J}_{\mu,3} \right), \]

\[ \hat{J}_{\mu,1}^E = \frac{1}{\sqrt{6}} \left( 2\hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,3} \right), \]

\[ \hat{J}_{\mu,2}^E = \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,2} - \hat{J}_{\mu,3} \right), \]

(6.3)

with \( \mu = +, -, 0 \). According to (6.2) we can construct four possible interactions that are quadratic in \( \hat{J}_{\mu,\gamma}^\Gamma \), three of which correspond to linear combinations of the terms in (2.14)

\[ T_{\pm}^{A_1} (A_1) = \frac{3}{2} N + \frac{1}{2} \sum_{i=1}^{3} H_i^M + \frac{1}{2} \sum_{i,j=1}^{3} \hat{V}_{ij} \]  

(6.4a)

\[ T_{\pm}^{A_1} (E) = 2N + \frac{1}{3} \left( 4 \sum_{i=1}^{3} H_i^M - \sum_{i,j=1}^{3} \hat{V}_{ij} \right) \]  

(6.4b)

\[ T_0^{A_1} (A_1) = \frac{9}{4} N^2 - \sum_{i=1}^{3} H_i^M - \sum_{i,j=1}^{3} \hat{H}_{ij} \]  

(6.4c)

while the fourth is not independent, since

\[ \hat{J}^2_{A_1} + \hat{J}^2_E = \sum_{i=1}^{3} \hat{J}_i^2 = \frac{3}{4} \hat{N} (\hat{N} + 2). \]  

(6.4d)

In addition to the operators in (6.2) which transform as \( A_1 \) under \( D_3 \), we can also construct other bilinear combinations with well-defined tensor properties,

\[ \hat{T}_1^E = \frac{1}{2} \left( \hat{J}_{-1,2}^E \hat{J}_{+2}^E - \hat{J}_{-1,1}^E \hat{J}_{+1}^E \right), \]

\[ \hat{T}_2^E = \frac{1}{2} \left( \hat{J}_{-1,1}^E \hat{J}_{+2}^E + \hat{J}_{-1,2}^E \hat{J}_{+1}^E \right), \]

\[ \hat{T}^{A_2} = \frac{i}{2} \left( \hat{J}_{-1,1}^E \hat{J}_{+2}^E - \hat{J}_{-1,2}^E \hat{J}_{+1}^E \right). \]

(6.5)

22
The operator \( \hat{T}^{A_2} \) is proportional to the intrinsic angular momentum operator of (5.17).

In lowest order (\textit{i.e.} quadratic in \( \hat{T}^\Gamma \)) there are two possible \( A_1 \) interactions, \((\hat{T}_1^E)^2 + (\hat{T}_2^E)^2\) and \((\hat{T}^{A_2})^2\). In order to interpret these interactions we take the harmonic limit of (6.5)

\[
\begin{align*}
\lim_{N \to \infty} \frac{1}{N} \hat{T}_1^E &= \hat{L}_x = \frac{1}{2} \left( b_{E_2}^\dagger b_{E_1} - b_{E_1}^\dagger b_{E_2} \right), \\
\lim_{N \to \infty} \frac{1}{N} \hat{T}_2^E &= \hat{L}_y = \frac{1}{2} \left( b_{E_1}^\dagger b_{E_2} + b_{E_2}^\dagger b_{E_1} \right), \\
\lim_{N \to \infty} \frac{1}{N} \hat{T}^{A_2} &= \hat{L}_z = \frac{i}{2} \left( b_{E_1}^\dagger b_{E_2} - b_{E_2}^\dagger b_{E_1} \right).
\end{align*}
\]

(6.6)

The operators \( \hat{L}_x, \hat{L}_y \) and \( \hat{L}_z \) close under the commutation relations of \( SU(2) \). In the harmonic limit \((\hat{T}^{A_2})^2\) corresponds to \( \hat{L}_z^2 = \hat{l}_z^2/4 \) (see eq. (5.14)) while \((\hat{T}_1^E)^2 + (\hat{T}_2^E)^2\) goes to \( \hat{L}_x^2 + \hat{L}_y^2 = \bar{L}^2 - \hat{L}_z^2 \) with \( \bar{L}^2 = \hat{n}_E (\hat{n}_E + 2)/4 \), corresponding to an anharmonic contribution to the \( E \) mode.

In the next order \textit{(i.e.} cubic in \( \hat{T}^\Gamma \)) we can first couple \( T^E_\gamma \) to \( E \) and then couple again the resulting operator to \( T^E_\gamma \) to obtain an \( A_1 \) operator,

\[
\hat{O}^{A_1} = \left( \hat{T}_2^E \hat{T}_2^E - \hat{T}_1^E \hat{T}_1^E \right) \hat{T}_1^E + \left( \hat{T}_1^E \hat{T}_2^E + \hat{T}_2^E \hat{T}_1^E \right) \hat{T}_2^E = \frac{1}{2} \left( \hat{T}_+^3 + \hat{T}_-^3 \right),
\]

(6.7)

where we have introduced \( \hat{T}_\pm = \hat{T}_1^E \pm i \hat{T}_2^E \), which in the harmonic limit reduce to the ladder operators \( \hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y \). In the harmonic limit the operator (6.8) has a clear physical interpretation: it couples states with \( \Delta L_z = \pm 3 \), or expressed in terms of the intrinsic angular momentum, it couples states with the same \( v_E \) and \( \Delta l = \pm 6 \). For this reason it splits the \( a_1 \) and \( a_2 \) vibrations that are associated with the \((v_{A_1}, v_{E}^{l=3})\) multiplet.

The explicit realization of \( \hat{O}^{A_1} \) in the AOSM can be obtained by expressing \( \hat{T}_+ \) (and \( \hat{T}_- = (\hat{T}_+)^\dagger \)) in terms of the \( \hat{J}_{\pm,i} \) operators through equations (6.5) and (6.3). The final
result is
\[
\hat{T}_+ = -\frac{1}{6} \left[ 2\hat{J}_{-1}\hat{J}_{+1} - \hat{J}_{-2}\hat{J}_{+2} - \hat{J}_{-3}\hat{J}_{+3}
+ \hat{J}_{-1}(\hat{J}_{+2} + \hat{J}_{+3}) - \hat{J}_{-2}(\hat{J}_{+1} - 2\hat{J}_{+3})
- \hat{J}_{-3}(\hat{J}_{+1} - 2\hat{J}_{+2}) \right]
+ \frac{i}{2\sqrt{3}} \left[ \hat{J}_{-1}(\hat{J}_{+2} - \hat{J}_{+3}) + \hat{J}_{-2}(\hat{J}_{+1} - \hat{J}_{+2})
+ \hat{J}_{-3}(\hat{J}_{+3} - \hat{J}_{+1}) \right].
\] (6.8)

In the next section we show that the interaction (6.7) is essential to describe the highly anharmonic molecule $H_3^+$. It should be clear that the AOSM can be applied in a similar way to molecules exhibiting arbitrary symmetry groups. We have thus presented a systematic procedure to construct, up to a certain order, all relevant interactions, based on the introduction of operators with well-defined tensorial properties under the point group (see e.g. equation (6.1)), which can then be combined into $D_{3h}$ scalar interactions.

7. Application to $H_3^+$, $Be_3$ and $Na_3^+$

In this section we apply the AOSM to $Na_3^+$, $Be_3$ and $H_3^+$. As mentioned in the Introduction, we have chosen these molecules because they exhibit a wide range of behavior, ranging from the very anharmonic spectrum of $H_3^+$ to the almost exact harmonic spectrum of $Na_3^+$.

According to the discussion presented in the previous section, the Hamiltonian
\[
\hat{\mathcal{H}} = \alpha \hat{\mathcal{H}}_{A_1} + \beta \hat{\mathcal{H}}_E + \gamma \hat{\mathcal{V}} + \delta \hat{\mathcal{V}}^2,
\] (7.1)
contains the main physical interactions that describe a $D_{3h}$-triatomic molecule, whose spectrum is close to the one generated by the Dunham expansion (4.3). As mentioned
before, the Dunham expansion implies a degeneracy between the \( a_1 \) and \( a_2 \) levels associated to the same quantum number \( l \), while the spectrum generated by (7.1) does lead to their splitting, although it is generally small. Experimentally this splitting is observed, even for molecules like Na\(^+\), in spite of its harmonic behavior. In the model Hamiltonian (7.1) this effect is produced by the \( \hat{H}_{A_1} \) operator, as can be seen from Fig.3.

We now consider the molecules H\(^+\), Be\(_3\) and Na\(^+\). The atoms in the first molecule are very light and the spectrum is highly anharmonic, a fact that is reflected by a strong splitting of the \( a_1, a_2 \) levels (200 cm\(^{-1}\) for \( V = 3 \)), as well as by a relatively large splitting of levels belonging to the same \((v_{A_1}, v_E)\) multiplet but with different value of \( l \) (220 cm\(^{-1}\) for \( V = 2 \)). This is in contrast with the case of Na\(^+\), where the splitting between the \( a_1 \) and \( a_2 \) levels is very small (0.11 cm\(^{-1}\) for \( V = 3 \)) as well as the \( l \)-dependent splitting (0.82 cm\(^{-1}\) for \( V = 2 \)). The molecule Be\(_3\) exhibits an intermediate behavior, although in this case an \( a_1, a_2 \) splitting is not present in the fitted data, since we have generated its spectrum from an \textit{ab initio} calculation where no splitting terms are included.\(^{15}\)

In Table V we present a least square fit calculation for H\(^+\), Be\(_3\) and Na\(^+\) up to three quanta, using the Hamiltonian (7.1) with \( \delta = 0 \). The standard deviation (rms) was taken to be

\[
\text{rms} = \sqrt{\frac{\sum (E_{exp}^i - E_{th}^i)^2}{n - n_p}},
\]

(7.2)

where \( n \) and \( n_p \) correspond to the number of fitted levels and parameters involved, respectively. From this calculation we find a large difference in the quality of the fit between H\(^+\) and the other two molecules. In Table VI we present the same calculations, but including the \( \hat{l}^2 \) interaction. We see that the difference in quality persists; while the Hamiltonian (7.1) is quite sufficient to describe the Be\(_3\) and Na\(^+\) molecules, we clearly require additional interactions to properly describe H\(^+\). This fact is in accordance with the work of Carter and Meyer,\(^{16}\) who are forced to include twice as many terms in the potential for H\(^+\) than for the Na\(^+\) molecule. The simplest possible set of such interactions in the
AOSM correspond to higher powers of the symmetry adapted operators (4.6) and (4.7). We propose
\[ \hat{\mathcal{H}}^2_{A_1}, \quad \hat{\mathcal{H}}^2_E, \quad \hat{\mathcal{H}}_{A_1E} \equiv \frac{\left( \hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_E + \hat{\mathcal{H}}_E \hat{\mathcal{H}}_{A_1} \right)}{2}. \] (7.3)

If we add this set of interactions to the Hamiltonian (7.1) in the energy fit for \( H^+ \) the rms deviation reduces to 15.74 cm\(^{-1}\). It is possible to further improve the fit by taking into account the interaction (6.7) in addition to the set (7.3). A more general algebraic Hamiltonian to describe \( D_{3h} \) molecules is then
\[ \hat{\mathcal{H}} = \alpha \hat{\mathcal{H}}_{A_1} + \beta \hat{\mathcal{H}}_E + \gamma \hat{\mathcal{V}} + \delta \hat{l}^2 + \alpha^{[2]} \hat{\mathcal{H}}^2_{A_1} + \beta^{[2]} \hat{\mathcal{H}}^2_E + \xi^{[2]} \hat{\mathcal{H}}_{A_1E} + \epsilon (\hat{T}^3_+ + \hat{T}^3_-). \] (7.4)

As mentioned before, the operator \( \hat{T}^3_+ + \hat{T}^3_- \) has the effect of splitting the \( a_1 \) and \( a_2 \) levels arising from the same angular momentum \( l \), which explains the need for this interaction in \( H^+ \). In Table VII we present the least square energy fit to \( H^+ \) using the Hamiltonian (7.4), with an rms deviation of 5.84 cm\(^{-1}\). We remark that in order to describe \( H^+ \) for higher phonon numbers we need to include higher order interactions. We believe, however, that this result is very encouraging. If we omit the purely anharmonic interaction \( \hat{\mathcal{V}} \) the rms increases to 24.37 cm\(^{-1}\), while carrying out the harmonic limit \( (N \to \infty) \), where \( \hat{\mathcal{V}} = 0 \), the rms obtained is 31.17 cm\(^{-1}\).

8. Conclusions

We have introduced the Anharmonic Oscillator Symmetry Model and applied it to a set of \( D_{3h} \)-triatomic molecules. The model is based on symmetry methods which systematically incorporate group theoretical techniques, providing a clear methodological procedure that can be applied to more complex molecules. We have introduced symmetry adapted operators that have a specific action over the function space. This is a general procedure
which gives rise to a clear physical interpretation of the interactions and has the additional advantage of considerably improving the convergence during the least square energy fit. Furthermore, based on the harmonic limit of the SU(2) algebra we have proposed a systematic approach to derive an algebraic realization of interactions given in configuration space. The model surmounts one of the main objections raised against the use of algebraic models, where it was not possible to obtain a direct correspondence with the configuration-space approaches. Although we have illustrated this procedure by means of the \( \hat{I}^2 \) interaction, the method can be used for arbitrary operators. For the general case when there is no information about the form of these interactions in configuration space, we have devised an algebraic procedure to derive them using their tensorial structure under the point group. The combination of the different methodologies leads to the AOSM, which can be applied in the same fashion to more complex molecules. We remark that the model can be extended in several ways. For example, Fermi resonances can be taking into account using perturbation theory, while the rotational degrees of freedom can be incorporated by coupling the vibrational wave functions to rotational states carrying the appropriate point symmetries.\(^{23,24}\)

We believe that the AOSM represents a systematic, simple but accurate alternative to configuration space methods, particularly for polyatomic molecules, where the integro-differential approaches are too complex to be applied or require very large numerical calculations. Since the model provides manageable wave functions, it is possible to evaluate the matrix elements of arbitrary physical operators, which have a simple representation in the algebraic space. A finer test for the model is to use these wave functions, for example, for the evaluation of infrared and Raman intensities. The transition operators can be constructed by applying our method to the configuration-space parametrizations, which correspond to the harmonic limit, \( N \to \infty \), or purely algebraically by using their tensorial
properties under the corresponding point group. The analysis of electromagnetic intensities, as well as the application of the model to other molecular systems will be presented in future publications.\textsuperscript{17,23}

**Acknowledgments**

We are grateful to P. Van Isacker and F. Iachello for his continuous interest and useful comments. This work was supported in part by the European Community under contract nr CI1*-CT94-0072, DGAPA-UNAM under project IN105194, CONACyT-México under project 400340-5-3401E and Spanish DGCYT under project PB92-0663.

**References**

1. J. Michael Hollas, *Modern Spectroscopy*, John Wiley 1992; Kazuo Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Wiley - Interscience publication, 1978.

2. Gerard Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, van Nostrand, New York, 1950.

3. E.B. Wilson, Jr., J.C. Decious and P. Cross, Molecular Vibrations, Dover, New York, 1980.

4. W.T. Raynes, P. Lazzeretti, R. Zanesi, A.J. Sadly and P.W. Fowler, Mol. Phys. 60 (1987) 509; G.D. Carney and R.N. Porter, J. Chem. Phys. 65 (1976) 3547.

5. D.L. Gray and A.G. Robiette, Mol. Phys. 37 (1979) 1901.

6. J.F. Ogilvie, J. Mol. Spect., 69 (1978) 169; W. Meyer and P. Botschwina, J. Chem. Phys., 84 (1986) 891.

7. F. Iachello, Chem. Phys. Lett. 78 (1981) 581; F. Iachello and R.D. Levine, J. Chem. Phys. 77 (1982) 3046.
8. F. Iachello, S. Oss and R. Lemus, J. Mol. Spect. **146** (1991) 56; Ibidem **149** (1991) 132.
9. F. Iachello and S. Oss, J. Mol. Spect. **142** (1990) 85.
10. O.S. van Roosmalen, I. Benjamin and R.D. Levine, J. Chem. Phys. **81** (1984) 5986.
11. F. Iachello and S. Oss, Phys. Rev. Lett. **66** (1991) 2976; Chem. Phys. Lett. **187** (1991) 500; F. Iachello and S. Oss. Chem. Phys. Lett. **205** (1993) 285; J. Chem. Phys. **99** (1993) 7337.
12. J.M. Arias, A. Frank, R. Lemus and F. Pérez-Bernal, Rev. Mex. Fís. **41** (1995) 728.
13. R. Lemus and A. Frank, J. Chem. Phys. **101** (1994) 8321; A. Frank and R. Lemus, Phys. Rev. Lett. **68** (1992) 413.
14. R. Bijker, A.E.L. Dieperink and A. Leviatan, Phys. Rev. A. **52** (1995) 2786.
15. A.P. Rendell, T.J. Lee and P.R. Taylor, J. Chem. Phys. **92** (1990) 7050.
16. S. Carter and W. Meyer, J. Chem. Phys. **93** (1990) 8902.
17. F. Pérez-Bernal, R. Bijker, A. Frank, R. Lemus and J.M. Arias, preprint, Chem-ph/96 03003.
18. Y. Alhassid, F. Gürsey and F. Iachello, Ann. of Phys. **148** (1983) 346.
19. A. Frank and P. Van Isacker, *Algebraic Methods in Molecular and Nuclear Structure Physics*, Wiley, New York, 1994.
20. S.L. Altmann and P. Herzig, *Point Group Theory Tables*, Clarendon Press, Oxford, 1994.
21. M. Hamermesh, *Group Theory and its Applications to Physical Problems*, Addison-Wesley, 1962.
22. K.T. Hecht, J. Mol. Spect. **5** (1960) 355.
23. J.K.G. Watson, J. Mol. Spect. **103** (1984) 350; Ibid, Can. J. Phys. **72** (1994) 238; J. Tennyson and J.R. Henderson, J. Chem. Phys. **91** (1989) 3815.
24. A. Frank, R. Lemus, J. Pérez-Bernal and J.M. Arias, to be published.
Figure Captions

Figure 1. Assignment of the $U^i(2)$ algebras for $D_{3h}$ triatomic molecules and the selection of the Cartesian coordinate system. The elements of the symmetry group $D_3$ are also indicated.

Figure 2. Eigenvalues of the operator $\hat{H}_E$ as a function of the number of bosons $N$ for (a) two phonons and (b) three phonons.

Figure 3. Eigenvalues of the operator $\hat{H}_{A_1}$ as a function of the number of bosons $N$ for (a) two phonons and (b) three phonons.

Figure 4. Eigenvalues of the operator $\hat{V}$ as a function of the number of bosons $N$ for two and three phonons.
Table I. Character table for the $D_3 \approx S_3$ group. The set $\{R_x, R_y, R_z\}$ represents the components of an axial vector.

$$
\begin{array}{cccc}
D_3 & E & C_3(2) & C_2(3) \\
A_1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 \\
E & 2 & -1 & 0 \\
\end{array}
$$

Basis functions:

- $2z^2 - x^2 - y^2$
- $z; R_z$
- $(x, y), (R_x, R_y)$
- $(zx, yz), (xy, x^2 - y^2)$

Table II. The $E$ irreducible representation of the generators of the $S_3$ group in the Cartesian basis of Table I.

$$
\begin{array}{ccc}
Irrep & (123) & (23) \\
S_3 & C_3 & C_2^3 & D_3 \\
E & \begin{pmatrix}
-\frac{1}{2} & -\frac{\sqrt{3}}{2} \\
\frac{\sqrt{3}}{2} & -\frac{1}{2}
\end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\end{array}
$$

Table III. Clebsch-Gordan coefficients $C(\mu \nu \Gamma; ij \gamma)$ for the $S_3$ group compatible with the irreps of Table II.

$$
\begin{array}{cccc}
\mu \times \nu & (ij) & A_2 \times E & (11) (12) \\
(\Gamma)_{\gamma} & C(\mu \nu \Gamma; ij \gamma) & (E)_1 & 0 & 1 \\
& & (E)_2 & -1 & 0
\end{array}
$$

$$
\begin{array}{cccccc}
E \times E & (11) & (12) & (21) & (22) \\
A_1 & 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} \\
A_2 & 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \\
(E)_1 & 1/\sqrt{2} & 0 & 0 & -1/\sqrt{2} \\
(E)_2 & 0 & -1/\sqrt{2} & -1/\sqrt{2} & 0
\end{array}
$$
Table IV. $D_3$ decompositions for two and three quanta.

| $v_{A_1}$ | $v_E$ | Irreps         | Dimension of the reducible representation |
|-----------|-------|----------------|-------------------------------------------|
| 2         | 0     | $A_1$          | 1                                         |
| 0         | 2     | $A_1 \oplus E$| 3                                         |
| 1         | 1     | $E$            | 2                                         |
|           |       |                | 6                                         |
| 3         | 0     | $A_1$          | 1                                         |
| 0         | 3     | $A_1 \oplus A_2 \oplus E$ | 4                   |
| 2         | 1     | $E$            | 2                                         |
| 1         | 2     | $A_1 \oplus E$| 3                                         |
|           |       |                | 10                                        |
Table V. Least square energy fit for H$^+_3$, Be$_3$ and Na$_3^+$. All energies are in cm$^{-1}$. We indicate the rms deviation (7.2) and the parameters obtained. The number of bosons $N$ was taken to be 30. The energy difference is given by $\Delta E = E_{th} - E_{exp}$, where $E_{exp}$ are taken from *ab initio* calculations.

| $(v_{A_1}v_{E_1})$ | Symmetry | $H^+_3$ | $Be_3$ | $Na^+_3$ |
|-------------------|-----------|---------|--------|----------|
|                   |           | $Exp.$ | $Exp.$ | $Exp.$ |
| $(01^1)$          | $e$       | $2521.27$ | $-0.17$ | $399.10$ | $4.09$ | $99.95$ | $1.68$ |
| $(10^0)$          | $a_1$     | $3178.32$ | $-29.32$ | $458.40$ | $0.25$ | $140.45$ | $2.16$ |
| $(02^0)$          | $a_1$     | $4777.02$ | $102.26$ | $782.40$ | $8.33$ | $198.90$ | $2.02$ |
| $(02^2)$          | $e$       | $4997.41$ | $-45.57$ | $794.40$ | $1.31$ | $199.72$ | $1.25$ |
| $(11^1)$          | $e$       | $5553.67$ | $-14.97$ | $845.10$ | $2.02$ | $239.29$ | $1.70$ |
| $(20^0)$          | $a_1$     | $6261.92$ | $-22.77$ | $907.60$ | $-0.04$ | $280.35$ | $1.66$ |
| $(03^1)$          | $e$       | $7003.49$ | $105.59$ | $1161.90$ | $3.91$ | $297.67$ | $0.25$ |
| $(03^3)$          | $a_1$     | $7282.52$ | $-102.30$ | $1185.90$ | $-13.85$ | $299.26$ | $-1.25$ |
| $(03^3)$          | $a_2$     | $7492.64$ | $-105.84$ | $1185.90$ | $-3.95$ | $297.67$ | $-1.36$ |
| $(12^0)$          | $a_1$     | $7769.09$ | $116.14$ | $1216.00$ | $9.71$ | $337.19$ | $-0.15$ |
| $(12^2)$          | $e$       | $7868.64$ | $-32.58$ | $1228.00$ | $-3.37$ | $337.94$ | $-0.86$ |
| $(21^1)$          | $e$       | $8486.90$ | $1.37$ | $1281.90$ | $-0.72$ | $378.06$ | $-0.91$ |
| $(30^0)$          | $a_1$     | $9251.42$ | $14.89$ | $1347.60$ | $-1.04$ | $419.70$ | $-1.49$ |

| $rms$ | 78.55 | 6.48 | 2.58 |
|-------|-------|------|------|
| $\alpha$ | 3148.996 | 458.653 | 142.608 |
| Parameters | $\beta$ | 2521.105 | 403.185 | 101.633 |
| | $\gamma$ | 3796.387 | 328.843 | 49.434 |

33
Table VI. Least square energy fit for $H_3^+$, $Be_3$ and $Na_3^+$ using the Hamiltonian (7.1). We show the energy differences $\Delta E = E_{th} - E_{exp}$. The values of the energies $E_{exp}$ are given in Table V.

| $(v_{A_i}v_{E_j})$ | Symmetry | $H_3^+$ $\Delta E$ | $Be_3$ $\Delta E$ | $Na_3^+$ $\Delta E$ |
|-------------------|----------|---------------------|-------------------|---------------------|
| (01$^1$)          | e        | -37.18              | 0.51              | 0.93                |
| (10$^0$)          | a$_1$    | -21.70              | 0.02              | 1.95                |
| (02$^0$)          | a$_1$    | -16.32              | -0.74             | 0.37                |
| (02$^2$)          | e        | -33.84              | 0.17              | 0.84                |
| (11$^1$)          | e        | -35.74              | 0.82              | 1.68                |
| (20$^0$)          | a$_1$    | -13.42              | -0.04             | 1.26                |
| (03$^1$)          | e        | 18.66               | -2.05             | -1.19               |
| (03$^3$)          | a$_1$    | 16.05               | -1.23             | -0.34               |
| (03$^3$)          | a$_2$    | -0.62               | 0.61              | -0.33               |
| (12$^0$)          | a$_1$    | 46.62               | 1.90              | -0.01               |
| (12$^2$)          | e        | -12.83              | -1.36             | 0.34                |
| (21$^1$)          | e        | -3.38               | 0.79              | -0.19               |
| (30$^0$)          | a$_1$    | 22.56               | -1.66             | -2.06               |

| rms | 30.15 | 1.24 | 1.25 |

| Parameters | $\alpha$ | 3156.616 | 458.911 | 142.396 |
|------------|----------|----------|--------|---------|
|            | $\beta$  | 2446.638 | 396.265 | 100.317 |
|            | $\gamma$ | 3131.825 | 209.744 | 21.312  |
|            | $\delta$ | -12.485  | -0.9533 | -0.1867 |
Table VII. Least square energy fit of the $H_3^+$ molecule using the Hamiltonian (7.6).

$$H_3^+$$

| $(v_{A_1} v_{E})$ | Symmetry | $\Delta E$ |
|------------------|----------|-----------|
| $(01^1)$         | $e$      | -1.55     |
| $(10^0)$         | $a_1$    | 0.42      |
| $(02^0)$         | $a_1$    | 7.48      |
| $(02^2)$         | $e$      | -5.69     |
| $(11^1)$         | $e$      | -0.61     |
| $(20^0)$         | $a_1$    | -0.11     |
| $(03^1)$         | $e$      | -4.46     |
| $(03^3)$         | $a_1$    | 3.18      |
| $(03^3)$         | $a_2$    | 2.44      |
| $(12^0)$         | $a_1$    | 0.66      |
| $(12^2)$         | $e$      | -5.0      |
| $(21^1)$         | $e$      | 4.07      |
| $(30^0)$         | $a_1$    | -1.23     |

$rms$ \hspace{1cm} 5.84 cm$^{-1}$

Parameters
\[ \alpha = 3193.600 \]
\[ \beta = 2507.157 \]
\[ \gamma = 2807.833 \]
\[ \delta = -13.439 \]
\[ \alpha^{[2]} = -14.855 \]
\[ \beta^{[2]} = -27.752 \]
\[ \xi^{[2]} = -28.043 \]
\[ \epsilon = -0.900 \]