

A symmetry adapted approach to molecular spectroscopy: the anharmonic oscillator symmetry model

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ABSTRACT. We apply the anharmonic oscillator symmetry model to the description of vibrational excitations in D_{3h} and T_d molecules. A systematic procedure can be used to establish the relation between the algebraic and configuration space formulations, by means of which new interactions are found in the algebraic model, leading to reliable spectroscopic predictions. We illustrate the method for the case of triatomic D_{3h} molecules and the T_d Be_4 -cluster.

RESUMEN. Utilizamos el modelo de simetría de osciladores anarmónicos para describir las excitaciones vibracionales en moléculas con simetría D_{3h} y T_d . Un procedimiento sistemático permite establecer la relación entre la formulación algebraica y la del espacio de configuración. Mediante esta conexión se encuentran nuevas interacciones en el modelo algebraico que dan lugar a predicciones espectroscópicas confiables. Ilustramos el método para el caso de moléculas triatómicas D_{3h} y para el cúmulo de berilio Be_4 con simetría tetraédrica.

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The study of molecular vibrational spectra [1] requires theoretical models in order to analyze and interpret the measurements [2]. These models range from simple parametrizations of the energy levels, such as the Dunham expansion [2], to *ab initio* calculations, where solutions of the Schrödinger equation in different approximations are sought [3-5]. In general, the latter involve the use of internal coordinates and the evaluation of force field constants associated to derivatives at the potential minima. While this method can be reliably applied to small molecules [6], it quickly becomes a formidable problem in the case of larger molecules, due to the size of their configuration spaces. New calculational tools to describe complex molecules are thus needed.

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]

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and certain non-linear triatomic molecules [9]. Although these were encouraging results, the model could not be extended to polyatomic molecules, due to the impossibility of incorporating the underlying discrete symmetries. This difficulty could 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 [10], later extended to describe the stretching vibrations of polyatomic molecules such as octahedral and benzene like molecules [11]. Recently the bending modes have also been included in the framework, which was subsequently applied to describe C_{2v} -triatomic molecules [12] and the lower excitations of tetrahedral molecules [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 [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.

Although the algebraic formulations have proved useful, several problems remained, most important of which is the absence of a clear connection to traditional methods. On the other hand, a related problem is the lack of a systematic procedure to construct all physically meaningful interactions in the algebraic space. In this paper we show that both these issues can be resolved by means of a general model for the analysis of molecular vibrational spectra, the anharmonic oscillator symmetry model (AOSM). In this approach it is possible to construct algebraic operators with well defined physical meaning, in particular interactions fundamental for the description of the degenerate modes present in systems exhibiting high degree of symmetry. The procedure to construct them takes full advantage of the discrete symmetry of the molecule and gives rise to all possible terms in a systematic fashion. The harmonic limit of the model provides a clear-cut connection between the algebraic scheme and the traditional analyses based on internal coordinates.

As a test for this approach we apply the AOSM to the Be_4 cluster [15] and to three D_{3h} triatomic molecular systems, namely H_3^+ , Be_3 and Na_3^+ [16]. Since small molecules can in general be well described by means of *ab initio* calculations [17, 18], we emphasize the basic purpose of this work. We have established an exact correspondence between configuration space and algebraic interactions by studying 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. In the case of Be_4 , a direct comparison with *ab initio* calculations will be presented. The application of these techniques to more complex systems, such as the methane molecules, is presently under investigation [19].

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

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D(e^{-\frac{2x}{a}} - 2e^{-\frac{x}{a}}), \quad (1)$$

whose eigenstates \mathcal{E} can be associated with $U(2) \supset SO(2)$ states [20]. In order to see how

this isomorphism comes about, consider the radial equation

$$\frac{1}{2} \left(-\frac{1}{r} \frac{d}{dr} r \frac{d}{dr} + \frac{\sigma^2}{r^2} + r^2 \right) \phi(r) = (N+1)\phi(r), \quad (2)$$

which corresponds to a two-dimensional harmonic oscillator (in units where $\hbar = \mu = e = 1$) associated to a $U(2)$ symmetry algebra [21]. By carrying out a change of variable

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

Eq. (2) transforms into

$$\left[-\frac{d^2}{d\rho^2} + \left(\frac{N+1}{2} \right)^2 (e^{-2\rho} - 2e^{-\rho}) \right] \phi(\rho) = -\left(\frac{\sigma}{2} \right)^2 \phi(\rho), \quad (3)$$

which can be identified with (1) after defining $x = \rho d$ and multiplying by $\hbar^2/2\mu d^2$, provided that

$$D = \frac{\hbar^2}{8\mu d^2} (N+1)^2, \quad (4)$$

$$\mathcal{E} = -\frac{\hbar^2}{2\mu d^2} m^2, \quad (5)$$

where we have defined $m = \sigma/2$. 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 (4), while m , the eigenvalue of the $SO(2)$ generator J_z , takes the values $m = \pm N/2, \pm(N-2)/2, \dots$. 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 (3-5) that the Morse Hamiltonian has the algebraic realization

$$\hat{H} = -\frac{\hbar^2}{2\mu d^2} \hat{J}_z^2 = -A \hat{J}_z^2. \quad (6)$$

In addition, the $U(2)$ algebra includes the raising and lowering operators \hat{J}_+, \hat{J}_- , which connect different energy states in (3), while the angular momentum operator is given by $\hat{J}^2 = \hat{N}(\hat{N}+2)/4$, as can be readily shown.

The Morse Hamiltonian (6) can be rewritten in the more convenient form

$$\hat{H}' = \hat{H} + A \frac{\hat{N}^2}{4} = \frac{A}{2} [(\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) - \hat{N}], \quad (7)$$

where we have used the relation $\hat{J}_z^2 = \hat{J}^2 - (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+)/2$ and added a constant term $A\hat{N}^2/4$ in order to place the ground state at zero energy. The parameters N and A appearing in (7) are related to the usual harmonic and anharmonic constants ω_e and $x_e\omega_e$

used in spectroscopy [7]. To obtain this relation it is convenient to introduce the quantum number

$$v = \frac{N}{2} - m, \quad (8)$$

which corresponds to the number of quanta in the oscillator [21]. In terms of v , the corresponding energy expression takes the form

$$E' = -A \left(m^2 - \frac{N^2}{4} \right) = -\frac{A}{2} (N + 1/2) + A(N + 1)(v + 1/2) - A(v + 1/2)^2, \quad (9)$$

from which we immediately obtain

$$\begin{aligned} \omega_e &= A(N + 1), \\ x_e \omega_e &= A. \end{aligned} \quad (10)$$

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

We now consider the $U_i(2) \supset SU_i(2) \supset SO_i(2)$ algebra, which is generated by the set $\{\hat{G}_i\} \equiv \{\hat{N}_i, \hat{J}_{+,i}, \hat{J}_{-,i}, \hat{J}_{0,i}\}$, satisfying the commutation relations

$$[\hat{J}_{0,i}, \hat{J}_{\pm,i}] = \pm \hat{J}_{\pm,i}, \quad [\hat{J}_{+,i}, \hat{J}_{-,i}] = 2\hat{J}_{0,i}, \quad [\hat{N}_i, \hat{J}_{\mu,i}] = 0, \quad (11)$$

with $\mu = \pm, 0$. As mentioned before, for the symmetric irreducible representation $[N_i, 0]$ of $U_i(2)$ one can show that the Casimir operator is given by [21] $\vec{J}_i^2 = \hat{N}_i(\hat{N}_i + 2)/4$, from which follows the identification $j_i = N_i/2$. The $SO_i(2)$ label is denoted by m_i .

In the algebraic approach each relevant interatomic interaction is associated with a $U_i(2)$ algebra [11]. As a specific example, we consider the Be_4 cluster, which has a tetrahedral shape. D_{3h} molecules can be similarly treated. In the Be_4 case there are six $U_i(2)$ algebras involved ($i = 1, \dots, 6$). The operators in the model are expressed in terms of the generators of these algebras, and the symmetry requirements of the tetrahedral group T_d can be readily imposed [13, 22]. The local operators $\{\hat{G}_i\}$ acting on bond i can be projected to any of the fundamental irreps $\Gamma = A_1, E$ and F_2 . Using the $\hat{J}_{\mu,i}$ generators (11) we obtain the T_d tensors

$$\hat{T}_{\mu,\gamma}^\Gamma = \sum_{i=1}^6 \alpha_{\gamma,i}^\Gamma \hat{J}_{\mu,i}, \quad (12)$$

where $\mu = \pm, 0$ and γ denotes the component of Γ . The explicit expressions are given by

$$\begin{aligned} \hat{T}_{\mu,1}^{A_1} &= \frac{1}{\sqrt{6}} \sum_{i=1}^6 \hat{J}_{\mu,i}, \\ \hat{T}_{\mu,1}^E &= \frac{1}{2\sqrt{3}} \left(\hat{J}_{\mu,1} + \hat{J}_{\mu,2} - 2\hat{J}_{\mu,3} + \hat{J}_{\mu,4} - 2\hat{J}_{\mu,5} + \hat{J}_{\mu,6} \right), \end{aligned}$$

$$\begin{aligned}
\hat{T}_{\mu,2}^E &= \frac{1}{2} (\hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,4} + \hat{J}_{\mu,6}), \\
\hat{T}_{\mu,1}^{F_2} &= \frac{1}{\sqrt{2}} (\hat{J}_{\mu,1} - \hat{J}_{\mu,6}), \\
\hat{T}_{\mu,2}^{F_2} &= \frac{1}{\sqrt{2}} (\hat{J}_{\mu,2} - \hat{J}_{\mu,4}), \\
\hat{T}_{\mu,3}^{F_2} &= \frac{1}{\sqrt{2}} (\hat{J}_{\mu,3} - \hat{J}_{\mu,5}).
\end{aligned} \tag{13}$$

The Hamiltonian operator can be constructed by repeated couplings of these tensors to a total symmetry A_1 , since it must commute with all operations in \mathcal{T}_d . This is accomplished by means of the \mathcal{T}_d -Clebsch-Gordan coefficients [13, 22, 23].

All calculations are carried out in a symmetry-adapted basis, which is projected from the local basis

$$\begin{array}{ccccccc}
U_1(2) \otimes \cdots \otimes U_6(2) \supset SO_1(2) \otimes \cdots \otimes SO_6(2) \supset SO(2) & & & & & & \\
\downarrow & & \downarrow & \downarrow & & \downarrow & \downarrow \\
|[N_1], \dots, [N_6]; v_1, \dots, v_6; V\rangle & & & & & &
\end{array} \tag{14}$$

in which each anharmonic oscillator is well defined. By symmetry considerations, $N_i = N$ for the six oscillators, $v_i = N_i/2 - m_i$ denotes the phonon number in bond i and $V = \sum_i v_i$ is the total number of phonons [13, 21]. The one-phonon states $V = 1$ are denoted by $|i\rangle$ with $v_i = 1$ and $v_{j \neq i} = 0$. Using the same projection technique as for the generators (13), we find the six fundamental modes

$${}^1\phi_\gamma^\Gamma = \sum_{i=1}^6 \alpha_{\gamma,i}^\Gamma |i\rangle. \tag{15}$$

The expansion coefficients are the same as in (13). The higher phonon states ${}^V\phi_\gamma^\Gamma$ can also be constructed using the Clebsch-Gordan coefficients of \mathcal{T}_d [13, 22]. Since all operators are expressed in terms of powers of the $U_i(2)$ generators, their matrix elements can be easily evaluated in closed form. The symmetry-adapted operators (13) and states (15) are the building blocks of the model. Note that for more complex molecules, the method allows the exact elimination of spurious states [19].

We now proceed to explicitly construct the Be_4 Hamiltonian. For interactions that are at most quadratic in the generators the procedure yields

$$\hat{H}_0 = \omega_1 \hat{\mathcal{H}}_{A_1} + \omega_2 \hat{\mathcal{H}}_E + \omega_3 \hat{\mathcal{H}}_{F_2} + b_2 \hat{\mathcal{V}}_E + b_3 \hat{\mathcal{V}}_{F_2}, \tag{16}$$

with

$$\begin{aligned}
\hat{\mathcal{H}}_\Gamma &= \frac{1}{2N} \sum_\gamma (\hat{T}_{-, \gamma}^\Gamma \hat{T}_{+, \gamma}^\Gamma + \hat{T}_{+, \gamma}^\Gamma \hat{T}_{-, \gamma}^\Gamma), \\
\hat{\mathcal{V}}_\Gamma &= \frac{1}{N} \sum_\gamma \hat{T}_{0, \gamma}^\Gamma \hat{T}_{0, \gamma}^\Gamma,
\end{aligned} \tag{17}$$

Note that we have not included $\hat{\mathcal{V}}_{A_1}$ in (16), since the combination

$$\sum_{\Gamma} (\hat{\mathcal{H}}_{\Gamma} + \hat{\mathcal{V}}_{\Gamma}) = \frac{1}{4N} \sum_i \hat{N}_i (\hat{N}_i + 2), \quad (18)$$

is a constant $3(N+2)/4$. The five interaction terms in Eq. (16) correspond to linear combinations of the ones obtained in lowest order in Refs. [11,13]. However, it is necessary to include interactions which are related to the vibrational angular momenta associated with the degenerate modes E and F_2 . These kind of terms is absent in the former versions of the model [11,13]. We now proceed to show how they can be obtained in the AOSM. In configuration space the vibrational angular momentum operator for the E mode is given by [24]

$$\hat{l}^{A_2} = -i \left(q_1^E \frac{\partial}{\partial q_2^E} - q_2^E \frac{\partial}{\partial q_1^E} \right), \quad (19)$$

where q_1^E and q_2^E are the normal coordinates associated to the E mode. This relation can be transformed to the algebraic space by means of the harmonic oscillator operators

$$b_{\gamma}^{\Gamma\dagger} = \frac{1}{\sqrt{2}} \left(q_{\gamma}^{\Gamma} - \frac{\partial}{\partial q_{\gamma}^{\Gamma}} \right), \quad b_{\gamma}^{\Gamma} = \frac{1}{\sqrt{2}} \left(q_{\gamma}^{\Gamma} + \frac{\partial}{\partial q_{\gamma}^{\Gamma}} \right), \quad (20)$$

to obtain

$$\hat{l}^{A_2} = -i (b_1^{E\dagger} b_2^E - b_2^{E\dagger} b_1^E). \quad (21)$$

Here $b_{\gamma}^E = \sum_i \alpha_{\gamma,i}^E b_i$, with a similar form for $b_{\gamma}^{\Gamma\dagger}$, while the $\alpha_{\gamma,i}^E$ can be read from (13). In order to find the algebraic expression for \hat{l}^{A_2} we first introduce a scale transformation in (11)

$$\bar{b}_i^{\dagger} \equiv \hat{J}_{-,i} / \sqrt{N_i}, \quad \bar{b}_i \equiv \hat{J}_{+,i} / \sqrt{N_i}. \quad (22)$$

The relevant commutator can be expressed as

$$[\bar{b}_i, \bar{b}_i^{\dagger}] = \frac{1}{N_i} [\hat{J}_{+,i}, \hat{J}_{-,i}] = \frac{1}{N_i} 2\hat{J}_{0,i} = 1 - \frac{2\hat{v}_i}{N_i}, \quad (23)$$

where

$$\hat{v}_i = \frac{\hat{N}_i}{2} - \hat{J}_{0,i}. \quad (24)$$

The other two commutators in (11) are not modified by (22). In the harmonic limit, which is defined by $N_i \rightarrow \infty$, Eq. (23) reduces to the standard boson commutator $[\bar{b}_i, \bar{b}_i^{\dagger}] = 1$. This limit corresponds to a contraction of $SU(2)$ to the Weyl algebra and can be used to

obtain a geometric interpretation of AOSM operators in terms of those in configuration space. In the opposite sense, Eq. (22) provides a procedure to construct the anharmonic representation of harmonic operators through the correspondence $b_i^\dagger \rightarrow \bar{b}_i^\dagger = \hat{J}_{-,i}/\sqrt{N_i}$ and $b_i \rightarrow \bar{b}_i = \hat{J}_{+,i}/\sqrt{N_i}$. Applying this method to the vibrational angular momentum (21) we find

$$\hat{l}^{A_2} = -\frac{i}{N} \left(\hat{J}_{-,1}^E \hat{J}_{+,2}^E - \hat{J}_{-,2}^E \hat{J}_{+,1}^E \right). \quad (25)$$

For the vibrational angular momentum $\hat{l}_\gamma^{F_1}$ associated with the F_2 mode we find a similar expression. The AOSM form of the corresponding Hamiltonian interactions is

$$\hat{H}_1 = g_{22} \hat{l}^{A_2} \hat{l}^{A_2} + g_{33} \sum_\gamma \hat{l}_\gamma^{F_1} \hat{l}_\gamma^{F_1}. \quad (26)$$

With this method we obtain an algebraic realization of arbitrary configuration space interactions. As a simple example, a one-dimensional harmonic oscillator Hamiltonian $\hat{H}_i = (b_i^\dagger b_i + b_i b_i^\dagger)/2$, transforms into

$$\frac{1}{2N} (\hat{J}_{-,i} \hat{J}_{+,i} + \hat{J}_{+,i} \hat{J}_{-,i}) = \frac{1}{N} (\hat{J}_i^2 - \hat{J}_{0,i}^2) = \hat{v}_i + 1/2 - \frac{\hat{v}_i^2}{N}, \quad (27)$$

where in the last step we used relation (24). The spectrum of (27) has an anharmonic correction, analogous to the quadratic term in the Morse potential spectrum. We are thus substituting harmonic oscillators by Morse oscillators in the AOSM.

A more interesting application is to use our model to fit the spectroscopic data of several polyatomic molecules. In the case of Be_4 the energy spectrum was analyzed by *ab initio* methods in [17], where force-field constants corresponding to an expansion of the potential up to fourth order in the normal coordinates and momenta were evaluated. We have generated the *ab initio* spectrum up to three phonons using the analysis in [24]. For the algebraic Hamiltonian we take [15]

$$\begin{aligned} \hat{H} = & \omega_1 \hat{\mathcal{H}}_{A_1} + \omega_2 \hat{\mathcal{H}}_E + \omega_3 \hat{\mathcal{H}}_{F_2} + X_{33} \left(\hat{\mathcal{H}}_{F_2} \right)^2 + X_{12} \left(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_E \right) + X_{13} \left(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_{F_2} \right) \\ & + g_{33} \sum_\gamma \hat{l}_\gamma^{F_1} \hat{l}_\gamma^{F_1} + t_{33} \hat{\mathcal{O}}_{33} + t_{23} \hat{\mathcal{O}}_{23}. \end{aligned} \quad (28)$$

The terms $\hat{\mathcal{O}}_{33}$ and $\hat{\mathcal{O}}_{23}$ represent the algebraic form of the corresponding interactions in [24] which are responsible for the splitting of the vibrational levels in the $(\nu_1, \nu_2^m, \nu_3^l) = (0, 0^0, 2^2)$ and the $(0, 1^1, 1^1)$ overtones [15].

In Table I we show the fit to Be_4 using the Hamiltonian (28). The fit includes all levels up to $V = 4$ phonon states and gives a r.m.s. deviation of 2.6 cm^{-1} , which can be considered of spectroscopic quality. In Table I we only show the results for $V \leq 3$ levels. We point out that in [17, 24] several higher order interactions are present which we have neglected. Since our model can be put into a one to one correspondence with the

TABLE I. Vibrational excitations of Be₄ using the algebraic Hamiltonian with parameters given in the text. The ab initio ($N \rightarrow \infty$) spectrum is generated with the parameters from [17]. The energies are given in cm⁻¹.

V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio $N \rightarrow \infty$	Present $N = 44$	V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio $N \rightarrow \infty$	Present $N = 44$
1	$(1, 0^0, 0^0)$	A_1	638.6	637.0	3	$(1, 0^0, 2^0)$	A_1	2106.8	2105.6
	$(0, 1^1, 0^0)$	E	453.6	455.0		$(1, 0^0, 2^2)$	E	2000.1	1999.8
	$(0, 0^0, 1^1)$	F_2	681.9	678.2		$(0, 3^1, 0^0)$	E	1341.3	1343.7
2	$(2, 0^0, 0^0)$	A_1	1271.0	1269.2	$(0, 3^3, 0^0)$	A_1	1355.5	1352.5	
	$(1, 1^1, 0^0)$	E	1087.1	1087.0	$(0, 3^3, 0^0)$	A_2	1355.5	1354.4	
	$(1, 0^0, 1^1)$	F_2	1312.6	1308.3	$(0, 2^{0,2}, 1^1)$	F_2	1565.5	1565.7	
	$(0, 2^0, 0^0)$	A_1	898.3	901.4	$(0, 2^2, 1^1)$	F_2	1584.4	1583.1	
	$(0, 2^2, 0^0)$	E	905.4	906.1	$(0, 2^2, 1^1)$	F_1	1578.5	1578.0	
	$(0, 1^1, 1^1)$	F_1	1126.7	1125.1	$(0, 1^1, 2^{0,2})$	E	1821.4	1821.6	
		F_2	1135.5	1134.1		E	1929.5	1929.0	
	$(0, 0^0, 2^0)$	A_1	1484.0	1483.0	$(0, 1^1, 2^2)$	A_2	1813.3	1813.1	
3	$(0, 0^0, 2^2)$	E	1377.3	1373.9	$(0, 1^1, 2^2)$	A_1	1830.8	1831.7	
		F_2	1434.1	1429.6	F_2	F_2	1874.4	1873.2	
	$(3, 0^0, 0^0)$	A_1	1897.0	1896.7	F_1	F_1	1883.2	1883.0	
	$(2, 1^1, 0^0)$	E	1714.3	1714.3	$(0, 0^0, 3^{1,3})$	F_2	2136.5	2134.2	
	$(2, 0^0, 1^1)$	F_2	1937.0	1933.7	F_2	F_2	2327.3	2326.9	
	$(1, 2^0, 0^0)$	A_1	1526.6	1529.2	$(0, 0^0, 3^3)$	F_1	2199.8	2197.1	
	$(1, 2^2, 0^0)$	E	1533.7	1532.8	A_1	A_1	2256.5	2254.4	
$(1, 1^1, 1^1)$	F_1	1752.2	1749.7						
	F_2	1761.0	1759.8						

configuration space calculations, it is in fact possible to improve the accuracy of the fit considerably, but we have used a simpler Hamiltonian than the one of [17,24]. When no *ab initio* calculations are available (or feasible) the AOSM approach can be used empirically, achieving increasingly good fits by the inclusion of higher order interactions [19].

The Be₄ Hamiltonian (28) preserves the total phonon-number V . This is a good approximation for this case according to the analysis of [17,24], but it is known that Fermi resonances can occur for certain molecules when the fundamental mode frequencies are such that (V, V') states with $V \neq V'$ are close in energy. These interactions can be introduced in the Hamiltonian but the size of the energy matrices grows very rapidly, so the best way to deal with this problem is through perturbation theory.

For \mathcal{D}_{3h} molecules we follow an analogous procedure, namely, we construct the \mathcal{D}_{3h} symmetry-adapted operators and states corresponding to (13) and (15) and carry out the building-up procedure to construct the Hamiltonian and higher phonon states [16]. Here we omit the details for lack of space and only present the fit to the energy spectrum [16,25].

TABLE II. Least-square energy fit for the vibrational excitations of H_3^+ , Be_3 and Na_3^+ . The energy differences $\Delta E = E_{\text{th}} - E_{\text{exp}}$ are given in cm^{-1} .

V	(ν_1, ν_2^l)	Γ	H_3^+ ΔE	Be_3 ΔE	Na_3^+ ΔE
1	$(0, 1^1)$	E	-1.55	0.51	0.93
	$(1, 0^0)$	A_1	0.42	0.02	1.95
2	$(0, 2^0)$	A_1	7.48	-0.74	0.37
	$(0, 2^2)$	E	-5.69	0.17	0.84
	$(1, 1^1)$	E	-0.61	0.82	1.68
	$(2, 0^0)$	A_1	-0.11	-0.04	1.26
3	$(0, 3^1)$	E	-4.46	-2.05	-1.19
	$(0, 3^3)$	A_1	3.18	-1.23	-0.34
	$(0, 3^3)$	A_2	2.44	0.61	-0.33
	$(1, 2^0)$	A_1	0.66	1.90	-0.01
	$(1, 2^2)$	E	-5.00	-1.36	0.34
	$(2, 1^1)$	E	4.07	0.79	-0.19
	$(3, 0^0)$	A_1	-1.23	-1.66	-2.06
r.m.s.			5.84	1.35	1.33
Parameters			8	4	4

In Table II we present AOSM fits to the spectra of Be_3 , Na_3^+ and H_3^+ up to three phonons. While remarkably accurate descriptions of the first two molecules can be achieved using a four-parameter Hamiltonian, we had to include four additional higher order terms in the H_3^+ Hamiltonian in order to properly describe this molecule. This is in accordance with the work of Carter and Meyer [18], who were forced to include twice as many terms in the potential energy surface for H_3^+ than for the Na_3^+ molecule. The H_3^+ ion is a very "soft" molecule which, due to the light mass of its atomic constituents carries out large amplitude oscillations from its equilibrium positions [18].

In another test of the model we studied the vibrational energies of two ozone isotopes, $^{16}\text{O}_3$ and $^{18}\text{O}_3$ [26]. A least-square fit to all published experimental levels (up to ten quanta) yields a r.m.s. deviation of 2.5 and 1.0 cm^{-1} , respectively.

A still finer test for the model is to use the wave functions to evaluate infrared and Raman transitions. The algebraic realization of the transition operators can be obtained from their expression in configuration space using the large N connection, or purely algebraically by their tensorial properties under the relevant point group [19]. We remark that the model can also be extended to include the rotational degrees of freedom, by coupling the vibrational wave functions to rotational states properly symmetrized to carry the point group representations [24].

The AOSM 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 define 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 fits. Based on the harmonic limit of the $SU(2)$ algebra we have found 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. 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 believe that the AOSM represents a systematic, simple but accurate alternative to the traditional 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. The study of electromagnetic intensities, as well as the application of the model to more complex molecules is currently under investigation [19].

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