Model of *n* Coupled Anharmonic Oscillators and Applications to Octahedral Molecules

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We propose an algebraic model of n coupled one-dimensional anharmonic oscillators and apply it to the study of the stretching modes of XY_6 octahedral molecules. We derive a new result on the theory of discrete groups and use it within the framework of the algebraic model to provide a four-parameter fit to the published vibrational energies of SF_6, WF_6, and UF_6 accurate within 0.9 cm^{-1}.

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One of the most interesting areas of current research in molecular physics is the study of the vibrational excited states of medium and large molecules. In view of the considerable amount of experimental activity in this area, one needs theoretical models within which to interpret experimental data. For medium-size and large molecules, models based directly on the solution of the many-body differential Schrödinger equation with interatomic potentials become rather cumbersome and difficult to apply. Similarly, straightforward Dunham-like expansions contain a large number of parameters which cannot be determined from the few available data. In this Letter we propose a model of n coupled anharmonic oscillators, which appears to describe vibrational stretching energies with considerable accuracy in terms of few parameters. In constructing this model, we use the isomorphism of the Lie algebra of U(2) with that of the one-dimensional Morse oscillator.[1] The eigenstates of the one-dimensional Schrödinger equation, $h\psi=\varepsilon\psi$, with a Morse potential[2]

$$h(p,x)=p^2/2\mu+D[1-\exp(-\alpha x)]^2\,, \tag{1}$$

can be put into one-to-one correspondence with the representations of $U(2)\supset O(2)$, characterized by the quantum numbers $|N,m\rangle$, with the proviso that one takes only the positive branch of m, i.e., $m=N,N-2,\ldots,1$ or 0 for $N=$odd or even ($N=$integer). The Morse Hamiltonian (1) corresponds in the U(2) basis to a simple Hamiltonian, $h=\varepsilon_0+AC$, where C is the invariant operator of O(2), with eigenvalues m^2-N^2. Thus, the eigenvalues of h are

$$\varepsilon=\varepsilon_0+A(m^2-N^2)\,, \qquad m=N,N-2,\ldots,1 \text{ or } 0 \;\; (N=\text{odd or even})\,. \tag{2}$$

Introducing the vibrational quantum number $v=(N-m)/2$, Eq. (2) can be rewritten as

$$\varepsilon=\varepsilon_0-4A(Nv-v^2)\,, \qquad v=0,1,\ldots,\frac{N}{2} \text{ or } \frac{N-1}{2} \;\; (N=\text{even or odd})\,. \tag{3}$$

The values of ε_0, A, and N are given in terms of μ, D, and α by $\varepsilon_0=-D$, $-4AN=\hbar\alpha(2D/\mu)^{1/2}$, $4A=-\hbar^2\alpha^2/2\mu$. One can immediately verify that these are the eigenvalues of the Morse oscillator.

Consider now a molecule with n bonds. For concreteness we treat here the case of XY_6 octahedral molecules, Fig. 1, with $n=6$. The model we propose is that in which each bond i is replaced by an algebra $U_i(2)$. Thus each bond represents a one-dimensional Morse oscillator, with Hamiltonian $h_i=\varepsilon_{0i}+A_iC_i$, where C_i is the invariant operator of $O_i(2)$ with eigenvalues $-4(N_iv_i-v_i^2)$. The bonds interact with each other with a bond-bond interaction. We consider two types of bond-bond interactions, C_{ij} and M_{ij}, that we call Casimir and Majorana interactions, for reasons which will become apparent below. The model Hamiltonian we consider is thus

$$H=E_0+\sum_{i=1}^{n}A_iC_i+\sum_{i<j}^{n}A_{ij}C_{ij}+\sum_{i<j}^{n}\lambda_{ij}M_{ij}\,. \tag{4}$$

The operator C_{ij} is diagonal with matrix elements

$$\langle N_i,v_i;N_j,v_j|C_{ij}|N_i,v_i;N_j,v_j\rangle=4[(v_i+v_j)^2-(v_i+v_j)(N_i+N_j)]\,, \tag{5}$$

while the operator M_{ij} has both diagonal and nondiagonal matrix elements,

$$\begin{aligned}
&\langle N_i,v_i;N_j,v_j|M_{ij}|N_i,v_i;N_j,v_j\rangle=v_iN_j+v_jN_i-2v_iv_j\,,\\
&\langle N_i,v_i+1;N_j,v_j-1|M_{ij}|N_i,v_i;N_j,v_j\rangle=-[v_j(v_i+1)(N_i-v_i)(N_j-v_j+1)]^{1/2}\,,\\
&\langle N_i,v_i-1;N_j,v_j+1|M_{ij}|N_i,v_i;N_j,v_j\rangle=-[v_i(v_j+1)(N_j-v_j)(N_i-v_i+1)]^{1/2}\,.
\end{aligned} \tag{6}$$

Equation (6) is a generalization to n bonds of the two-bond model of Ref. 3. The operators C_{ij} and M_{ij} have been called Casimir and Majorana, respectively, because of their group-theoretic properties. They are the invar-

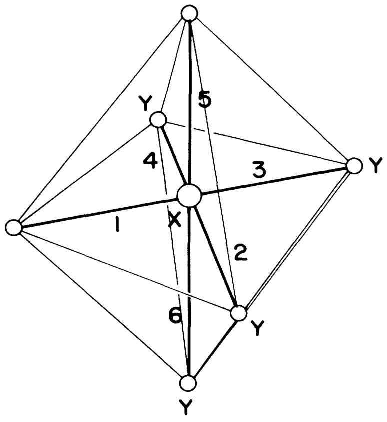

FIG. 1. Schematic representation of a XY_6 octahedral molecule.

iant operators of the combined algebras $O_{ij}(2)$ and $U_{ij}(2)$ in the group lattice

$$\begin{tikzcd} & O_i(2)\otimes O_j(2) \arrow[dr, dash] & \\ U_i(2)\otimes U_j(2) \arrow[ur, dash] \arrow[dr, dash] & & O_{ij}(2) \\ & U_{ij}(2) \arrow[ur, dash] & \end{tikzcd} . \qquad (7)$$

Their physical meaning can be seen from the matrix elements (5) and (6). The operators C_{ij} describe anharmonic terms of the type $v_i v_j$, while the operators M_{ij} describe interbond couplings which, in configuration space, are of the type $r_i r_j$, where r_i and r_j are the displacement vectors of bonds i and j from their equilibrium values. In this Letter we show, by explicit calculation, that the model Hamiltonian (4) provides a description of stretching modes of polyatomic molecules that equals or surpasses that of any previously considered model. In addition, we derive an important result on the theory of discrete groups which opens the way for applications to molecules of any symmetry.

As an example, we consider the case of XY_6 octahedral molecules. We number the bonds 1 to 6 as in Fig. 1. It is seen from the figure that all bonds are equivalent. Thus, we must have $N_i = N$, $A_i = A$ (any i), and $A_{ij} = A'$ (any i and j). In addition, we expect that off-diagonal couplings between adjacent bonds (for example, $ij = 12, 14, \ldots$) are different than off-diagonal couplings between opposite bonds (for example, $ij = 13, \ldots$). We thus take, for octahedral molecules,

$$\begin{aligned} &\lambda_{12}=\lambda_{14}=\lambda_{15}=\lambda_{16}=\lambda_{23}=\lambda_{25}=\lambda_{26} \\ &\quad =\lambda_{34}=\lambda_{35}=\lambda_{36}=\lambda_{45}=\lambda_{46}\equiv\lambda\,, \\ &\lambda_{13}=\lambda_{24}=\lambda_{56}\equiv\lambda'\,. \end{aligned} \qquad (8)$$

Equations (4), (5), (6), and (8) provide then a description of the stretching modes of octahedral molecules in terms of four parameters, A, A', λ, λ'. [The value of N can be fixed from the anharmonicity of the single bond, using Eq. (3).] If the molecule were to have a different symmetry, different values of the λ_{ij}'s should be used, reflecting this symmetry.

Equations (4)-(8) do much more than just provide a description of energy levels. For a molecule with a definite symmetry (here the octahedral symmetry O_h), states must be characterized by representations of the corresponding discrete group. (For O_h these are the symmetry species A_{1g}, E_g, F_{1u}, F_{2g}, and F_{2u}.) Any calculation of vibrational levels of octahedral molecules must impose this constraint. This is usually done by constructing symmetry-adapted states.[4] As discussed in Ref. 4, for large molecules this construction is an extremely difficult task. However, one can use the algebraic properties of the Majorana operator M_{ij}, i.e., that it is the invariant operator of $U_{ij}(2)$, and the fact that the representations of the unitary groups are related to those of the permutation groups[5] to obtain the important mathematical result that diagonalization of appropriate linear combinations of the M_{ij}'s produce states that automatically transform as representations of the appropriate point group. This result, to our knowledge previously unknown, allows one to use, in a straightforward way, algebraic models for the description of molecules of any symmetry. In the case discussed here, the appropriate operators are

$$\begin{aligned} &S=\sum_{i<j}^{6} M_{ij}, \quad S'=\sum_{i<j}^{6} c_{ij} M_{ij}\,, \\ &c_{12}=c_{14}=c_{15}=c_{16}=c_{23}=c_{25}=c_{26} \\ &\quad =c_{34}=c_{35}=c_{36}=c_{45}=c_{46}=1\,, \\ &c_{13}=c_{24}=c_{56}=0\,. \end{aligned} \qquad (9)$$

Diagonalization of S produces states that are representations of the permutation group of six objects, S_6, while diagonalization of S' produces states that transform as representations of the octahedral group O_h. This result, that at first sight appears very surprising, can be easily verified by diagonalizing S' and computing the characters of the representations carried by the resulting eigenstates. In view of it, diagonalization of the Hamiltonian appropriate to octahedral molecules,

$$\begin{aligned} &H=E_0+AC+A'C'+\lambda S+\lambda' S'\,, \\ &C=\sum_{i=1}^{6} C_i, \quad C'=\sum_{i<j}^{6} C_{ij}\,, \end{aligned} \qquad (10)$$

automatically produces states that transform as representations of O_h.

As an example, we report in Table I the results of fits to the published vibrational levels of $^{32}S^{19}F_6$, $^{184}W^{19}F_6$, and $^{238}U^{19}F_6$ taken from Ref. 4. The values of the four parameters A, A', λ, λ' (and of N) are also shown in the table. The three fundamental frequencies A_{1g}, E_g, and F_{1u} are denoted by ν_1, ν_2, and ν_3, respectively. We have

TABLE I. Comparison between calculated and observed energy levels of SF_6, WF_6, and UF_6.[a]

		SF_6		WF_6		UF_6	
$\vert\nu_1\nu_2\nu_3>$	Symm	E_{calc}	E_{obs}	E_{calc}	E_{obs}	E_{calc}	E_{obs}
|010>	E_g	645.36	643.35	678.00	678.20	533.52	534.10
|100>	A_{1g}	774.09	774.54	772.14	772.10	666.37	667.10
|001>	F_{1u}	948.19	948.10	712.60	712.40	625.72	625.50
|020>	A_{1g}	1288.18		1354.07	1354.00	1065.86	1066.50
	E_g	1289.48		1354.83	1354.00 [b]	1066.33	1066.30
|110>	E_g	1416.72		1448.25		1198.51	1197.00
|200>	A_{1g}	1546.75		1543.02		1331.85	
|011>	F_{1u}	1588.31	1588.10	1387.17	1387.10	1157.11	1156.90
	F_{2u}	1593.66		1390.21		1159.00	
|101>	F_{1u}	1719.65	1719.59	1482.76	1482.80	1290.74	1290.90
|002>	E_g	1890.91	1889.05	1422.29	1422.40	1249.41	
	A_{1g}	1890.91	1889.05	1422.42	1422.40 [b]	1249.44	
	F_{2g}	1896.49	1896.53	1424.81	1422.40 [b]	1251.19	
|030>	E_g	1929.74		2028.94		1597.47	
	A_{1g}	1932.27		2030.44		1598.40	
	A_{2g}	1932.46		2030.53		1598.42	
|120>	A_{1g}	2056.90		2122.45		1729.47	
	E_g	2058.08		2123.18		1729.93	
|210>	E_g	2186.66		2217.23		1862.62	
|021>	F_{1u}	2226.38	2227.50	2060.05		1687.50	1687.50
	F_{2u}	2232.66		2063.67		1689.68	
	F_{1u}	2237.27		2066.29		1691.33	
|300>	A_{1g}	2317.97		2312.63		1996.46	
|111>	F_{1u}	2357.14		2155.66		1820.73	1821.00
	F_{2u}	2362.27		2158.44		1822.63	
|201>	F_{1u}	2489.66	2488.40	2251.65		1954.89	1955.00
|012>	E_g	2525.59		2093.28		1778.67	
	A_{1g}	2525.59		2093.42		1778.70	
	F_{1g}	2534.21		2097.55		1781.41	
	A_{2g}	2536.47		2099.48		1782.46	
	E_g	2536.48		2099.69		1782.47	
	F_{2g}	2539.33		2100.49		1783.27	
|102>	E_g	2659.96		2190.44		1913.11	
	A_{1g}	2659.97		2190.66		1913.18	
	F_{2g}	2665.21		2192.93		1914.86	
|003>	F_{1u}	2828.14	2827.55	2129.22		1871.15	1874.60
	F_{2u}	2839.31	2840.35	2134.10		1874.65	
	F_{1u}	2839.31	2839.04	2134.20		1874.67	
	A_{2u}	2844.90	2845.28	2136.63		1876.42	
	N	180		200		250	
	A	-0.915		-0.289		-0.141	
	A'	-0.017		-0.068		-0.053	
	λ	-0.119		-0.078		-0.089	
	λ'	+0.722		+0.008		+0.096	

[a] All values in cm^{-1}, except N which is dimensionless. Observed values taken from compilation in Ref. 4.

[b] Estimated values not included in the fit.

reported in this table the energies of states up to three quanta of vibration, but we can obviously calculate overtone and combination frequencies up to any number of quanta. The model Hamiltonian (10) appears to describe the energy levels with good accuracy, irrespective of the fact that the three molecules of Table I have behavior ranging from "local" (UF_6) to "normal" (SF_6). In view of the high accuracy of the fits, we think that the calculations reported in the table can be used safely to predict the energies of unknown states. Comparing with other models, we do not know, at the present time, of any other calculation that can account, with the same number of parameters, for the observed overtone and combination frequencies with better accuracy.

In conclusion, we have suggested an algebraic model of n coupled one-dimensional anharmonic oscillators which describes stretching vibrations of large molecules quite accurately. The model is based on the use of Morse oscillators and it is thus related to the model of Halonen and Child[4] and others[6] who have successfully used Morse oscillator potentials for polyatomic molecules. However, by making use of algebraic methods, we solve two problems: (i) that connected with the convergence of integration in Schrödinger-like pictures and, most importantly, (ii) that connected with the construction of representations of the discrete group appropriate to the molecule under consideration. The latter result arises from the use of coupling operators, Majorana-type operators, which have the appropriate transformation properties under the discrete group (here O_h). To obtain this result within other schemes, for example, that in which each bond i is replaced by a force constant $f_r^{(i)}$, and then interbond couplings $f_{rr'}^{(i,j)}$ are added, is no easy task, as discussed, for example, in Ref. 4. In this paper, we have applied the model to the study of octahedral molecules, but it can be equally well applied to the study of other molecules, for example, tetrahedral molecules, such as methane CH_4, or even more complex molecules, such as benzene C_6H_6, polymers such as polyacetylene ($n \rightarrow \infty$), and anharmonic solids. The model can also be used to compute intensities of infrared and Raman transitions. The corresponding results will be reported in a longer paper.

Finally, we note that algebraic models have been used in the past to treat structural problems of molecules. However, they have dealt almost exclusively with harmonic situations. The model discussed here addresses the question of anharmonic effects. The order of magnitude of these effects can be seen from Table I by considering the triplet of states $|002\rangle$. The observed splitting is 6.48 cm^{-1}. The calculated splitting is 5.58 cm^{-1}. The splittings increase for higher overtone and combination bands and it is in the correct description of these bands that the power of the algebraic method lies. This has been demonstrated recently by detailed analysis of molecules of lower symmetry.[7] The novel aspects of the present Letter are, in addition to the inclusion of bond anharmonicities, Eq. (4), and interbond couplings, Eq. (8), (i) the discovery of operators S, Eq. (9), which allow a simple construction of symmetry-adapted states, and (ii) the explicit demonstration of the accurate description of the stretching vibrations of polyatomic molecules that one can obtain within the framework of algebraic models.

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