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Iachello, F.; Levine, R. D.

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Algebraic approach to molecular rotation-vibration spectra. I. Diatomic molecules

F. Iachello, and R. D. Levine

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Algebraic approach to molecular rotation-vibration spectra.

I. Diatomic molecules

F. Iachello

*Wright Nuclear Structure Laboratory, Yale University, New Haven, Connecticut 06511
and Kernfysisch Verneller Instituut, Rijksuniversiteit Groningen, The Netherlands*

R. D. Levine

*The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem, Israel
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An algebraic approach to molecular rotation-vibration spectra, similar to that used in the analysis of nuclear rotation-vibration spectra, is suggested. The spectrum generating algebra appropriate to diatomic molecules $U(4)$ is constructed. Its two dynamical symmetries $O(4)$ and $U(3)$ are discussed and their relation to rigid and nonrigid structures is investigated. It is shown how other properties, such as intensities of dipole radiation and state-to-state excitation probabilities, can be evaluated.

I. INTRODUCTION

A simple analysis of molecular rotation-vibration spectra is provided by the Dunham expansion.¹ This is an expansion of the energy levels in terms of vibration-rotation quantum numbers. For diatomic molecules, for example, this yields

$$E(v, J) = \sum_{i,j} y_{i,j} (v + \frac{1}{2})^i [J(J+1)]^j. \quad (1.1)$$

The coefficients $y_{i,j}$ are obtained by a fit to the experimental energy levels. This expansion does not contain any information about the wave functions of individual states. Thus matrix elements of operators cannot be directly calculated.

A more sophisticated analysis is provided by the potential approach. Here energy levels are obtained by solving the Schrödinger equation with an interatomic potential. The potential V is expanded in terms of interatomic variables. For diatomic molecules, for example, a possible expansion is²

$$V(r) = \sum_n a_n \left(\frac{r-r_0}{b} \right)^n. \quad (1.2)$$

The coefficients a_n are obtained either by a fit to the experimental energy levels or, if available, by a fit to a theoretically calculated potential. The solution of the Schrödinger equation also provides wave functions $\psi(\mathbf{r})$ from which matrix elements of various operators can be calculated. In the potential approach, all manipulations are either differentiations or integrations.

In this article we would like to suggest a third possible approach to the analysis of molecular rotation-vibration spectra, based on algebraic (rather than differential) techniques. Our suggestion is stimulated by the success that a similar approach has had in the description of rotation-vibration spectra of nuclei.^{3,4} The basic idea is that of expanding the Hamiltonian (and other operators) in terms of a set of boson creation (and annihilation) operators characterizing the normal modes of the system. We shall call, in the following sections, these boson-like degrees of freedom "vibrons" and refer to the approach we propose as "vibron model." Con-

trary to the potential approach, all manipulations here are algebraic.

The purposes we have in mind are several.

(i) Many authors have emphasized the occurrence of both rigid and nonrigid molecules⁵; the algebraic approach we intend to pursue contains both limits.

(ii) For diatomic molecules, the solution of the Schrödinger equation with a potential $V(r)$ is very simple; thus, not much is gained by using an algebraic approach. For tri- and polyatomic molecules this is no longer the case; the use of algebraic techniques here gives rise to considerable simplifications.

(iii) For comparison with experiments on laser multiphoton excitation⁶ and excitation in atom-molecule and molecule-molecule collision,⁷ one needs to calculate state-to-state excitation probabilities [in diatomic molecules, for example, the probability $P_{v,J \rightarrow v',J'}$ to go from an initial (v, J) to a final (v', J') rotation-vibration state]; these are difficult to calculate in a potential approach. The use of algebraic techniques provides here too some simplifications.

(iv) Surprisal analysis of these excitation probabilities has demonstrated that a simple parametrization of them is often possible⁸; this simplicity appears to be related to the occurrence of dynamical symmetries.⁹ As will be shown below, the study of dynamical symmetries within the framework of an algebraic approach is straightforward.

Although the most important use of the algebraic techniques may be in the study of complex molecules, we shall in this article concentrate our attention only on diatomic molecules. Our purpose here is to introduce these techniques in the field of molecular physics. Subsequent publications will deal with tri- and polyatomic molecules. A preliminary, brief, version of this work has already appeared.^{10,11}

II. VIBRON MODEL

In this section, we introduce the basic ingredients of our algebraic approach, which we call "vibrons," and

write down the Hamiltonian (and other operators) in terms of them.

A. Boson calculus

A particularly convenient way to construct a spectrum generating algebra (SGA) for systems with a finite number of bound rotation-vibration states is through the use of a set of boson creation (b_α^\dagger) and annihilation (b_α) operators. The index $\alpha = 1, \dots, n$; the dimension n is related to the dimension u of the space in which the rotation-vibrations act by $n = u + 1$. This statement will be clarified in the following subsection where explicit examples of the spaces u will be constructed. The operators b_α^\dagger , b_α are assumed to satisfy Bose commutation relations

$$[b_\alpha, b_{\alpha'}^\dagger] = \delta_{\alpha\alpha'}, \quad [b_\alpha, b_{\alpha'}] = 0, \quad [b_\alpha^\dagger, b_{\alpha'}^\dagger] = 0. \quad (2.1)$$

All operators are expanded in bilinear products of the boson operators b_α^\dagger , b_α . For example, the Hamiltonian H is written as

$$H = h_0 + \sum_{\alpha\alpha'} \epsilon_{\alpha\alpha'} b_\alpha^\dagger b_{\alpha'} + \frac{1}{2} \sum_{\alpha\alpha'\beta\beta'} u_{\alpha\alpha'\beta\beta'} b_\alpha^\dagger b_{\alpha'} b_\beta^\dagger b_{\beta'} + \dots, \quad (2.2)$$

where h_0 , $\epsilon_{\alpha\alpha'}$, $u_{\alpha\alpha'\beta\beta'}$, ... are free parameters that characterize the system under study. Given h_0 , $\epsilon_{\alpha\alpha'}$, $u_{\alpha\alpha'\beta\beta'}$, ..., the eigenvalues and eigenstates of H are found by diagonalizing it in an appropriate basis:

$$B: b_\alpha^\dagger \dots b_{\alpha'}^\dagger |0\rangle. \quad (2.3)$$

The construction of the basis is simplified by the use of the theory of Lie groups.¹² The n^2 bilinear products

$$G_{\alpha\alpha'} = b_\alpha^\dagger b_{\alpha'} \quad (2.4)$$

generate the unitary group in n dimensions $U(n)$. Since the operators b_α^\dagger (b_α) satisfy Bose commutation relations, the basis states (2.3) must be totally symmetric. The appropriate basis is thus provided by the totally symmetric representations of the group $U(n)$, characterized by the total number N of bosons. Following the usual notation, we shall denote these representations either by

$[N]$ or by the corresponding Young tableau

$$[N] \equiv \overbrace{\square \square \dots \square}^{N \text{ boxes}}. \quad (2.5)$$

Introducing the generators (2.4), the Hamiltonian (2.2) can be rewritten as

$$H = h_0 + \sum_{\alpha\alpha'} \epsilon_{\alpha\alpha'} G_{\alpha\alpha'} + \frac{1}{2} \sum_{\alpha\alpha'\beta\beta'} u_{\alpha\alpha'\beta\beta'} G_{\alpha\alpha'} G_{\beta\beta'} + \dots, \quad (2.6)$$

i. e., as a sum of products of generators of $U(n)$. We shall call the part containing one generator, the one-body part, that containing the product of two generators, the two-body part, etc.

The major advantage of the algebraic technique is that the calculation of any physical property is reduced to algebraic manipulation either of the boson operators b_α^\dagger , b_α or of the generators $G_{\alpha\alpha'}$. This is a (sometimes) tedious but straightforward procedure.

B. Boson operators for molecular rotation-vibration spectra

Rotation-vibration spectra in nuclei arise from the fact that the nuclear surface may acquire a *quadrupole* deformation (Fig. 1). The number of degrees of freedom characterizing a quadrupole shape is $u=5$. These can be chosen, for example, as the two variables characterizing the intrinsic shape, usually called β and γ , and the three Euler angles characterizing the orientation of the deformed body in space θ_1 , θ_2 , and θ_3 (Bohr variables¹³). It has been suggested that the corresponding spectra may be analyzed by introducing *six* boson operators.¹⁴ The corresponding group structure (called "dynamical group") is thus $U(6)$.

Rotation-vibration spectra in diatomic molecules arise from the fact that the two atoms in the molecule may be separated by a distance r (*dipole* deformation), as shown in Fig. 1. The number of degrees of freedom characterizing a dipole shape is $u=3$. These can be chosen, for example, as the components of \mathbf{r} in spheri-

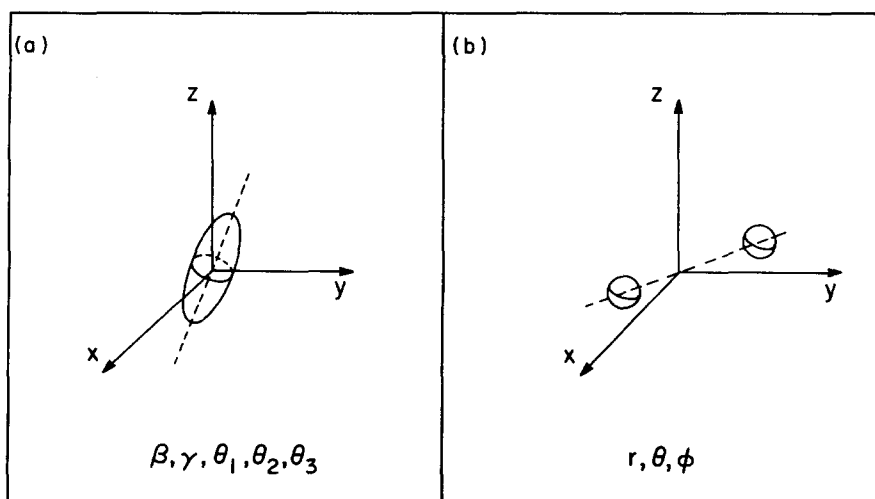


FIG. 1. Schematic representation of the geometric structure of nuclei (a) and diatomic molecules (b).

cal coordinates r , θ , and ϕ . Correspondingly, it has been suggested¹⁰ that the corresponding dynamical group is $U(4)$, generated by four creation and annihilation operators.

It is interesting to note that, had we considered vibrational spectra in one dimension ($u=1$), which are of the monopole type (only one degree of freedom x), we would have introduced two boson operators, with dynamical group $U(2)$. For a fixed boson number N one can consider $SU(2)$ instead of $U(2)$, whose algebra is isomorphic to that of $SO(3)$. This dynamical algebra was considered by Levine and Wulfman¹⁵ in their description of the excitations of the one-dimensional Morse oscillator. These authors constructed the algebra using quasispin generators Q_+ , Q_- , Q_0 . The construction of the algebra using the boson calculus employed here is an alternative form, known as Schwinger representation,¹⁶ and is, in turn, related to the algebraic approach to the one-dimensional Morse oscillator discussed by Berrondo and Palma.¹⁷ The dynamical algebra $U(4)$ we suggest is thus, on the one hand, the simplest generalization of the Levine-Wulfman algebra $U(2)$ and, on the other hand, a simplification of the algebra $U(6)$ used in the description of nuclear rotation-vibration spectra. The algebra $U(4)$ is related to the rotation-vibration spectra of a three-dimensional Morse oscillator, as will be discussed below.

Since the states of the system we want to describe are characterized by good values of the angular momentum J and parity P , the boson operators b_α^\dagger , b_α must have definite transformation properties under rotations and reflections. We, therefore, divide the four boson operators b_α^\dagger into a scalar having quantum numbers $J^P = 0^+$, denoted by σ^\dagger , and a vector having quantum numbers $J^P = 1^-$, denoted by π_μ^\dagger . The index μ labels the projections of this vector on an axis: $\mu = 0, \pm 1$. The transformation properties of the operator σ^\dagger under rotations are the same as those of the spherical harmonic Y_0^0 (a constant), while those of π_μ^\dagger are the same as those of the spherical harmonics Y_μ^1 . The commutation properties of the four creation operators σ^\dagger , π_μ^\dagger with the corresponding annihilation operators σ , π_μ are

$$\begin{aligned} [\sigma, \sigma^\dagger] &= 1, & [\sigma, \sigma] &= 0, & [\sigma^\dagger, \sigma^\dagger] &= 0, \\ [\pi_\mu, \pi_\mu^\dagger] &= \delta_{\mu\mu'}, & [\pi_\mu, \pi_{\mu'}] &= 0, & [\pi_\mu^\dagger, \pi_{\mu'}^\dagger] &= 0, \\ [\sigma, \pi_\mu^\dagger] &= 0, & [\sigma, \pi_\mu] &= 0, & [\sigma^\dagger, \pi_\mu^\dagger] &= 0, & [\sigma^\dagger, \pi_\mu] &= 0. \end{aligned} \quad (2.7)$$

C. Calculation of spectra

In calculating the spectrum of a given diatomic molecule, one begins by specifying the Hamiltonian H . In

$$\begin{aligned} H = & \hbar_0 + e_1^{(1)}[\sigma^\dagger \times \bar{\sigma}]_0^{(0)} + e_2^{(1)}[\pi^\dagger \times \bar{\pi}]_0^{(0)} + e_3^{(2)}\{[\pi^\dagger \times \pi^\dagger]^{(0)} \times [\bar{\pi} \times \bar{\pi}]^{(0)}\}_0^{(0)} + e_4^{(2)}\{[\pi^\dagger \times \pi^\dagger]^{(2)} \times [\bar{\pi} \times \bar{\pi}]^{(2)}\}_0^{(0)} + e_5^{(2)}\{[\pi^\dagger \times \pi^\dagger]^{(0)} \\ & \times [\bar{\sigma} \times \bar{\sigma}]^{(0)} + [\sigma^\dagger \times \sigma^\dagger]^{(0)} \times [\bar{\pi} \times \bar{\pi}]^{(0)}\}_0^{(0)} + e_6^{(2)}\{[\sigma^\dagger \times \sigma^\dagger]^{(0)} \times [\bar{\sigma} \times \bar{\sigma}]^{(0)}\}_0^{(0)} + e_7^{(2)}\{[\pi^\dagger \times \sigma^\dagger]^{(1)} \times [\bar{\pi} \times \bar{\sigma}]^{(1)}\}_0^{(0)} + \dots \end{aligned} \quad (2.13)$$

Here the coefficients $e_i^{(k)}$ are some linear combinations of the coefficients $\epsilon_{\alpha\alpha'}$, $u_{\alpha\alpha'\beta\beta'}$ appearing in Eq. (2.2), and we have used the fact that the Hamiltonian H must be Hermitian.

the potential approach it has been found convenient to expand the potential $V(r)$ into a set of known functions (1.2). Similarly, in the algebraic approach it is convenient to expand H in powers of generators G of the dynamical algebra. This expansion is written, in general, in (2.6). We now write down explicitly this expansion for the special case of molecular rotation-vibration spectra. In order to do this, we first note that H is a scalar under rotations. Thus, in constructing products of operators, we must form scalars. We have said above that the creation operators σ^\dagger and π_μ^\dagger transform under rotations as Y_0^0 and Y_μ^1 . One can show that, in general, if creation operators transform as spherical tensors under rotations, the annihilation operators do not. However, it is easy to construct operators that do. For an annihilation operator of multipolarity l , the corresponding operator that transforms as a spherical tensor is

$$\bar{b}_{l,\mu} = (-)^{l-\mu} b_{l,-\mu}. \quad (2.8)$$

This gives

$$\bar{\sigma} = \sigma, \quad \bar{\pi}_\mu = (-)^{1-\mu} \pi_{-\mu}. \quad (2.9)$$

Although there is no need to introduce $\bar{\sigma}$ since $\bar{\sigma} = \sigma$, we shall still do so in the following discussion in order to keep formulas symmetric.

Spherical tensors can be combined together to give other spherical tensors using the rules of angular momentum coupling. For the tensor product of two operators $t_{l,\mu}$ and $t_{l',\mu'}$, it is convenient to introduce the notation¹⁸

$$[t_l \times t_{l'}]_k^{(k)} = \sum_{\mu,\mu'} \langle l\mu l'\mu' | k\rangle t_{l,\mu} t_{l',\mu'}, \quad (2.10)$$

where $\langle l\mu l'\mu' | k\rangle$ is a Clebsch-Gordan coefficient. For example,

$$[\pi^\dagger \times \pi^\dagger]_k^{(2)} = \sum_{\mu,\mu'} \langle 1\mu 1\mu' | 2k\rangle \pi_\mu^\dagger \pi_{\mu'}^\dagger. \quad (2.11)$$

Similarly, one can introduce, for the scalar product of two operators $t_{l,\mu}$ and $u_{l,\mu}$, the notation¹⁸

$$(t_l \cdot u_l) = (-)^l \sqrt{2l+1} [t_l \times u_l]_0^{(0)} = \sum_{\mu} (-)^\mu t_{l,\mu} u_{l,-\mu}. \quad (2.12)$$

Since H is a scalar, only some terms survive in the expansion (2.2). For example, in the one-body part of H , terms of the type $\sigma^\dagger \bar{\pi}_\mu$ and $\pi_\mu^\dagger \bar{\sigma}$ will not be allowed since these products have angular momentum one. When written explicitly, the expansion (2.2) reads

The final step in calculating the spectrum is to assign the total number of bosons (vibrons) N . This number plays for $U(4)$ the same role that the number k plays in the algebraic treatment of the one-dimensional Morse

oscillator discussed by Levine and Wulfman.¹⁵ We shall call it “(three-dimensional) reduced anharmonicity.” Given N and H , the spectrum is obtained by diagonalizing H in the space of the totally symmetric representations $[N]$ of $U(4)$. It is interesting to note that within this space the Hamiltonian (2.13) can be further simplified. In fact, since H conserves the total number of vibrons

$$N = n_\sigma + n_\tau, \tag{2.14}$$

i. e.,

$$[H, N] = 0, \tag{2.15}$$

one can eliminate either n_σ or n_τ from Eq. (2.13). Consider, for example, the one-body terms $e_1^{(1)}, e_2^{(1)}$. Since the number operators can be written as

$$\begin{aligned} n_\sigma &= [\sigma^\dagger \times \bar{\sigma}]_0^{(0)}, \\ n_\tau &= \sqrt{3} [\pi^\dagger \times \bar{\pi}]_0^{(0)}, \end{aligned} \tag{2.16}$$

the two one-body terms can be rewritten as

$$\begin{aligned} e_1^{(1)}[\sigma^\dagger \times \bar{\sigma}]_0^{(0)} + e_2^{(1)}[\pi^\dagger \times \bar{\pi}]_0^{(0)} \\ = e_1^{(1)}N + (e_2^{(1)} - \sqrt{3} e_1^{(1)})[\pi^\dagger \times \bar{\pi}]_0^{(0)}. \end{aligned} \tag{2.17}$$

In the space $[N]$, the first term $e_1^{(1)}N$ is just a constant and thus it can be absorbed into h_0 . A similar treatment of the two-body terms allows one to rewrite H as

$$\begin{aligned} H = h_0' + e_1^{(1)}[\pi^\dagger \times \bar{\pi}]_0^{(0)} + e_2^{(2)}\{[\pi^\dagger \times \pi^\dagger]^{(0)} \times [\bar{\pi} \times \bar{\pi}]^{(0)}\}_0^{(0)} \\ + e_2^{(2)}\{[\pi^\dagger \times \pi^\dagger]^{(2)} \times [\bar{\pi} \times \bar{\pi}]^{(2)}\}_0^{(0)} + e_3^{(2)}\{[\pi^\dagger \times \pi^\dagger]^{(0)} \\ \times [\bar{\sigma} \times \bar{\sigma}]^{(0)} + [\sigma^\dagger \times \sigma^\dagger]^{(0)} \times [\bar{\pi} \times \bar{\pi}]^{(0)}\}_0^{(0)} + \dots, \end{aligned} \tag{2.18}$$

with

$$\begin{aligned} h_0' &= h_0 + e_1^{(1)}N + e_4^{(2)}N^2, \\ e_1^{(1)} &= e_2^{(1)} - \sqrt{3} e_1^{(1)} + 2\sqrt{3}(1-N)e_4^{(2)} + (N-1)e_5^{(2)}, \\ e_1^{(2)} &= e_1^{(2)} + e_4^{(2)} - e_5^{(2)}/\sqrt{3}, \\ e_2^{(2)} &= e_2^{(2)} + \sqrt{5} e_4^{(2)} - (\sqrt{5}/\sqrt{3})e_5^{(2)}, \\ e_3^{(2)} &= e_3^{(2)}. \end{aligned} \tag{2.19}$$

There are thus five independent parameters $h_0', e_1^{(1)}, e_1^{(2)}, e_2^{(2)}$, and $e_3^{(2)}$ that describe the Hamiltonian (2.18) up to second order.

There is still another equivalent form of rewriting the Hamiltonian (2.18). Introducing the operators

$$\begin{aligned} J_\mu^{(1)} &= \sqrt{2} [\pi^\dagger \times \bar{\pi}]_\mu^{(1)}, \\ D_\mu^{(1)} &= [\pi^\dagger \times \bar{\sigma} + \sigma^\dagger \times \bar{\pi}]_\mu^{(1)}, \end{aligned} \tag{2.20}$$

in addition to the operator n_τ of (2.16), the Hamiltonian H can be rewritten, up to two-body terms, as

$$H = h_0'' + e_1''^{(1)}n_\tau + e_1''^{(2)}n_\tau^2 + e_2''^{(2)}J^2 + e_3''^{(2)}D^2, \tag{2.21}$$

where the coefficients $h_0'', e_1''^{(1)}, e_1''^{(2)}$ are again some linear combination of those in Eq. (2.19). The operators J and D have the physical meaning of the angular momentum and dipole moment operators, respectively.

The calculation of the rotation-vibration spectrum of a diatomic molecule is then done by diagonalizing H , in one of its forms, in an appropriate basis. This, in general, must be done numerically and a computer program has been written by van Roosmalen¹⁹ to do this diagonalization. This program is available on request. The construction of this computer program is simplified by the use of group theory, as will be discussed below.

D. Calculation of electromagnetic transition rates

In addition to energy levels, one wishes often to calculate other properties, such as electromagnetic transition rates. This is done in the algebraic approach as follows. Consider, for example, the emission or absorption of dipole radiation. The appropriate operator transforms as a vector under rotations and reflections ($J^P = 1^-$). Thus, its expansion in terms of boson (vibron) operators can be written as

$$\begin{aligned} T_\mu^{(1)} = t_1^{(1)}[\sigma^\dagger \times \bar{\pi} + \pi^\dagger \times \bar{\sigma}]_\mu^{(1)} + t_2^{(1)}\{[\sigma^\dagger \times \sigma^\dagger]^{(0)} \times [\bar{\sigma} \times \bar{\pi}]^{(1)} + [\pi^\dagger \times \sigma^\dagger]^{(1)} \times [\bar{\sigma} \times \bar{\sigma}]^{(0)}\}_\mu^{(1)} \\ + t_3^{(1)}\{[\pi^\dagger \times \pi^\dagger]^{(0)} \times [\bar{\sigma} \times \bar{\pi}]^{(1)} + [\pi^\dagger \times \sigma^\dagger]^{(1)} \times [\bar{\pi} \times \bar{\pi}]^{(0)}\}_\mu^{(1)} + t_4^{(1)}\{[\pi^\dagger \times \pi^\dagger]^{(2)} \times [\bar{\sigma} \times \bar{\pi}]^{(1)} + [\pi^\dagger \times \sigma^\dagger]^{(1)} \times [\bar{\pi} \times \bar{\pi}]^{(2)}\}_\mu^{(1)} + \dots. \end{aligned} \tag{2.22}$$

In the potential approach, the electromagnetic transition operators are usually expanded in powers of r^{20} :

$$T_\mu^{(1)} = d_0 Y_\mu^{(1)} + d_1 (r - r_0) Y_\mu^{(1)} + \dots \tag{2.23}$$

For excitation of low-lying vibrational states, retaining only the linear term in Eq. (2.23) is a reasonably good approximation. However, for excitation of high-lying states this is no longer the case, since a more realistic form of the dipole operator is²⁰

$$T_\mu^{(1)} = [r^\nu \exp(-r/r^*)] Y_\mu^{(1)}, \quad \nu \geq 1, \quad r^* \approx r_0. \tag{2.24}$$

As will be shown below, the expansion (2.22) is somewhat more general than Eq. (2.23). However, even in the algebraic approach, the linear term alone $t_1^{(1)}$ will not be sufficient to describe excitations of the high-

lying vibrational states and higher order terms must be added.

Similarly, for emission and absorption of quadrupole ($J^P = 2^+$) radiation, one considers the operator

$$T_\mu^{(2)} = t_1^{(2)}[\pi^\dagger \times \bar{\pi}]_\mu^{(2)} + \dots \tag{2.25}$$

Electromagnetic transition rates can be calculated by taking matrix elements of the appropriate operators [Eqs. (2.22) or (2.25)] between initial and final state, e. g.,

$$t_{if,\mu}^{(1)} = \langle \psi_f | T_\mu^{(1)} | \psi_i \rangle. \tag{2.26}$$

The wave functions ψ_i and ψ_f are obtained from the diagonalization of the Hamiltonian H and can be written in the form

$$|\psi\rangle = \sum_{n_r} c_{n_r} (\sigma^\dagger)^{N-n_r} (\rho^\dagger)^{n_r} |0\rangle. \quad (2.27)$$

Thus, the computation of the matrix elements in Eq. (2.26) involves only some straightforward algebraic manipulation of the boson operators. The program written by van Roosmalen¹⁹ also calculates, in addition to energy levels, matrix elements of transition operators.

It is interesting to note that, introducing the operator

$$Q_\mu^{(2)} = [\pi^\dagger \times \tilde{\pi}]_\mu^{(2)} \quad (2.28)$$

in addition to the operators n_r , $J_\mu^{(1)}$, and $D_\mu^{(1)}$, the operator (2.22) can be written as

$$T_\mu^{(1)} = t_1^{(1)} D_\mu^{(1)} + t_2^{(1)} [n_r \times D^{(1)} + D^{(1)} \times n_r]_\mu^{(1)} + t_3^{(1)} [J^{(1)} \times D^{(1)} - D^{(1)} \times J^{(1)}]_\mu^{(1)} + t_4^{(1)} [Q^{(2)} \times D^{(1)} + D^{(1)} \times Q^{(2)}]_\mu^{(1)} + \dots, \quad (2.29)$$

where the coefficients $t_{1,2,3,4}^{(1)}$ are some linear combinations of the coefficients $t_{1,2,3,4}^{(1)}$ appearing in Eq. (2.22). The physical meaning of the operator $Q_\mu^{(2)}$ is that of the quadrupole moment operator. Because of the last two terms, the expansion (2.29) is more complex than Eq. (2.23).

Finally, we note that the transition operators discussed in this section are the generalization to three dimensions of the transition operators Q_\pm discussed in Ref. 15.

III. DYNAMICAL SYMMETRIES

One of the major advantages of the algebraic approach is that it allows one to construct, in some special cases, analytic expressions for all observable quantities. These special cases correspond to dynamical symmetries of the Hamiltonian H . Although the analytic solutions rarely describe the experimental situation very accurately, they are very useful since they provide simple examples that can be studied easily. Furthermore, dynamical symmetries appear to play a major role in collision processes.⁹

The technique used to find analytic solutions of an eigenvalue problem with group structure G is as follows. In general, the Hamiltonian H contains all the generators of G . However, suppose that H contains only invariant operators of a complete chain of groups

$$G \supset G' \supset \dots \quad (3.1)$$

Then the problem can be solved analytically, since the chain (3.1) provides a basis in which H is diagonal. In the case of molecular rotation-vibration spectra $G \equiv U(4)$. In order to find all possible chains of groups appropriate to this problem, one must remember that states are characterized by a good value of the angular momentum J . Thus, among the subgroups of G we must have the ordinary rotation group $O(3)$. Accordingly, there are only two possible chains of subgroups of $G = U(4)$:

$$\begin{aligned} \text{(I)} \quad & U(4) \supset O(4) \supset O(3) \supset O(2), \\ \text{(II)} \quad & U(4) \supset U(3) \supset O(3) \supset O(2). \end{aligned} \quad (3.2)$$

The group $O(2)$ corresponds to rotations around the z axis.

In addition to providing two possible dynamical symmetries, the two group chains are useful in providing two possible bases in which the most general Hamiltonian (2.18) can be diagonalized. Either can be used for numerical calculations, since both are complete and orthonormal. The program ROTVIB¹⁹ makes use of chain II since, as discussed below, matrix elements of all operators can be easily evaluated in this chain.

A. Labeling of states

In using the chains [Eq. (3.2)] the first problem to solve is that of a complete labeling of states. This is a straightforward group theoretical problem¹² and we give only the results.

For chain I the labels are (i) a quantum number N , the total vibron number, characterizing the totally symmetric irreducible representations of $U(4)$, as discussed in Eq. (2.5); (ii) a quantum number ω characterizing the totally symmetric representations of $O(4)$, which can take the values $\omega = N, N-2, N-4, \dots, 1$ or 0 for $N = \text{odd}$ or even; (iii) a quantum number J (the angular momentum) characterizing the representations of $O(3)$, where $J = \omega, \omega-1, \dots, 0$, and (iv) a quantum number M (the z component of the angular momentum) characterizing the representations of $O(2)$, where $-J \leq M \leq J$. Thus, the complete labeling of the states for chain I is

$$\begin{array}{cccc} U(4) \supset O(4) \supset O(3) \supset O(2) & & & \\ \downarrow & \downarrow & \downarrow & \downarrow \\ |N, \omega, J, M\rangle. & & & \end{array} \quad (3.3)$$

For chain II the labels are (i) a quantum number N characterizing the representations of $U(4)$, as above; (ii) a quantum number n_r characterizing the representations of $U(3)$, where $n_r = N, N-1, \dots, 0$; (iii) a quantum number J characterizing the representations of $O(3)$, where $J = n_r, n_r-2, \dots, 1$ or 0 for $n_r = \text{odd}$ or even; and (iv) a quantum number M characterizing the representations of $O(2)$, where (as above) $-J \leq M \leq J$. Thus, the complete labeling of states for chain II is

$$\begin{array}{cccc} U(4) \supset U(3) \supset O(3) \supset O(2) & & & \\ \downarrow & \downarrow & \downarrow & \downarrow \\ |N, n_r, J, M\rangle. & & & \end{array} \quad (3.4)$$

We remark that chain II is very convenient for numerical diagonalizations of the most general Hamiltonian H . In fact, in this chain, the first four terms in Eq. (2.18) are diagonal, and one needs only to calculate the matrix elements of the last term. These are given by

$$\begin{aligned} \langle N, n_r + 2, J, M | \{ [\pi^\dagger \times \pi^\dagger]^{(0)} \times [\tilde{\sigma} \times \tilde{\sigma}]_0^{(0)} \} | N, n_r, J, M \rangle \\ = (1/\sqrt{3}) \sqrt{(N-n_r)(N-n_r-1)} \sqrt{(n_r+J+3)(n_r-J+2)}. \end{aligned} \quad (3.5)$$

B. Energy levels

Suppose now that the Hamiltonian H can be written in terms only of invariant operators (Casimir operators) of one of the two chains [Eq. (3.2)]. We begin by considering chain I. In this case, the corresponding Hamiltonian, up to two-body terms, can be written as

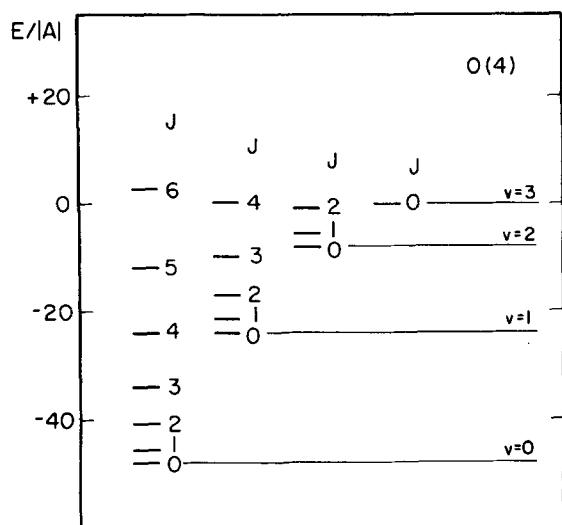


FIG. 2. Schematic representation of a spectrum with $O(4)$ symmetry. The energy levels are calculated using Eq. (3.10) with $N=6$, $F=0$, $B=-1.2A$, and A negative.

$$H^{(1)} = F + A c_2(04) + B c_2(03), \quad (3.6)$$

where F , A , and B are free parameters. We have used F instead of D (Ref. 10) in order not to confuse it with the dipole operator (2.20). The Casimir operators of $O(2)$ have not been included since they appear only if the molecule is placed in an external field that splits the various z components. Lie groups may have linear, quadratic, ..., invariant operators.¹² We use a notation where c_1 denotes a linear operator, c_2 a quadratic operator, etc. Since the orthogonal groups $O(4)$, $O(3)$ do not have linear invariant operators, only the quadratic ones have been included. In terms of the operators of Eq. (2.20), these have the simple form

$$\begin{aligned} c_2(04) &= D^2 + J^2, \\ c_2(03) &= J^2. \end{aligned} \quad (3.7)$$

Thus, this special case corresponds to the vanishing of the coefficients $e_1^{(1)}$, $e_1^{(2)}$ in Eq. (2.21). The Hamiltonian $H^{(1)}$ can be diagonalized in the basis I. Its eigenvalues are

$$E^{(1)}(N, \omega, J, M) = F + A\omega(\omega + 2) + BJ(J + 1). \quad (3.8)$$

In obtaining Eq. (3.8) we have made use of the explicit form of the eigenvalues of the Casimir operators of the orthogonal group¹²:

$$\begin{aligned} \langle c_2(04) \rangle &= \omega(\omega + 2), \\ \langle c_2(03) \rangle &= J(J + 1). \end{aligned} \quad (3.9)$$

In order to see the structure of the resulting spectrum, it is convenient to introduce a quantum number $v = (N - \omega)/2$, $v = 0, 1, \dots, N/2$ or $(N - 1)/2$, for $N = \text{even}$ or odd . The eigenvalue expression (3.8) can then be written as

$$\begin{aligned} E(N, v, J, M) &= F + (N^2 + 4N + 3)A - 4(N + 2)A(v + \frac{1}{2}) \\ &+ 4A(v + \frac{1}{2})^2 + BJ(J + 1). \end{aligned} \quad (3.10)$$

The structure of the corresponding spectrum for $N=6$ is shown in Fig. 2. Since the spectrum scales with $|A|$

we have preferred to plot $E/|A|$ instead of E . As one can see from the figure, drawn for A negative, $F=0$, and $B=-1.2A$, Eq. (3.10) describes the spectrum typical of a rigid diatomic molecule. Comparing Eq. (3.10) with the Dunham expansion (1.1), one can see that a dynamical symmetry with only one- and two-body terms in H , corresponds to a Dunham expansion with four coefficients y_{00} , y_{10} , y_{20} , and y_{01} . Furthermore, the y_{10} and y_{20} coefficients satisfy the relation $y_{10}/y_{20} = -(N + 2)$. Because of the relation

$$\begin{aligned} v &= \frac{N - \omega}{2}, \quad \omega = N, N - 2, \dots, 1 \text{ or } 0; \\ N &= \text{odd or even}, \end{aligned} \quad (3.11)$$

one can see that the total vibron number N (reduced anharmonicity) is related to the maximum number of bound vibrational states by

$$N = 2v_{\text{max}} \text{ or } N = 2v_{\text{max}} + 1, \quad N = \text{even or odd}. \quad (3.12)$$

It is also interesting to note that the energy levels of the three-dimensional Morse oscillator with

$$V(r) = V_0 \{ \exp[-2a(r - r_0)] - 2 \exp[-a(r - r_0)] \} \quad (3.13)$$

can be written, in lowest approximation, as in Eq. (3.10) with

$$\begin{aligned} F + A(N^2 + 4N + 3) &= -V_0, \\ -4A(N + 2) &= \hbar a(2V_0/m)^{1/2}, \\ A &= -\frac{\hbar^2}{8m} a^2, \\ B &= \frac{\hbar^2}{2mr_0^2}. \end{aligned} \quad (3.14)$$

Thus, the $O(4)$ dynamical symmetry describes, to some approximation, the energy levels of a three-dimensional Morse oscillator. This correspondence has been further investigated by van Roosmalen and Dieperink²¹ and by Levit and Smilansky.²²

We next come to the case in which the Hamiltonian H can be written in terms only of invariant operators of chain II of Eq. (3.2). It then can be written as

$$H^{(11)} = F + \epsilon c_1(U3) + \alpha c_2(U3) + \beta c_2(O3), \quad (3.15)$$

where F , ϵ , α , and β are free parameters. Both the linear and quadratic Casimir operators of $U(3)$ have been included, since unitary groups have both linear and quadratic invariants.¹² These operators have the simple form

$$\begin{aligned} c_1(U3) &= n_r, \\ c_2(U3) &= n_r^2 + 3n_r. \end{aligned} \quad (3.16)$$

This special case thus corresponds to the vanishing of $e_3^{(2)}$ in Eq. (2.21). The Hamiltonian (3.15) is diagonal in the basis II. Its eigenvalues are

$$E^{(11)}(N, n_r, J, M) = F + \epsilon n_r + \alpha n_r(n_r + 3) + \beta J(J + 1). \quad (3.17)$$

The structure of the corresponding spectrum for $N=6$ is shown in Fig. 3. Since in this case the energy levels scale with ϵ , we have plotted in Fig. 3 E/ϵ rather than E . The figure corresponds to the choice $F = -6.54\epsilon$, $\alpha = \beta = 0.01\epsilon$.

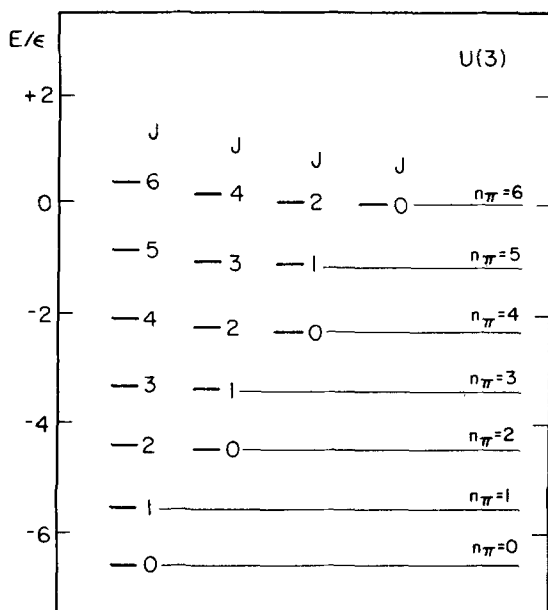


FIG. 3. Schematic representation of a spectrum with $U(3)$ symmetry. The energy levels are calculated using Eq. (3.17) with $N=6$, $F=-6.54\epsilon$, $\alpha=\beta=0.01\epsilon$, and ϵ positive.

It is interesting to note that several three-dimensional potentials have spectra that approximately correspond to Eq. (3.17). Among these we mention the Pöschl-Teller potential

$$V(r) = -V_0/ch^2ar \quad (3.18)$$

and the Woods-Saxon potential

$$V(r) = -V_0/\{1 + \exp[a(r-r_0)]\} \quad (3.19)$$

In order to compare the energy spectra corresponding to the two limiting cases I and II, it is convenient to consider the rigidity parameter γ introduced by Berry⁵

$$\gamma = 2E_r/E_v, \quad (3.20)$$

where E_r and E_v are the energies of the first rotational and first vibrational state. Using Eqs. (3.8) and (3.17), we find in case I

$$\gamma^{(I)} = -B/AN, \quad (3.21)$$

while in case II

$$\gamma^{(II)} = (\epsilon + 4\alpha + 2\beta)/(\epsilon + 5\alpha). \quad (3.22)$$

Since N is usually large, while the other coefficients are of the same order of magnitude, one has

$$(I) \gamma^{(I)} \ll 1, \quad (II) \gamma^{(II)} \approx 1. \quad (3.23)$$

Thus, limit I, is more appropriate for discussing rigid molecules, while limit II is more appropriate for discussing nonrigid molecules. Indeed, for $\alpha=0$ and $\beta=0$, $H^{(II)}$ is the Hamiltonian of a cutoff three-dimensional isotropic harmonic oscillator, and Amar, Kellman, and Berry²³ have already suggested the use of the group $U(3)$ in order to describe nonrigid molecules.

The analysis presented above has been limited to Hamiltonians with only one- and two-body terms. Inclusion of higher order terms leads to energy eigen-

value expressions with a larger number of terms. For example, in the limit of an $O(4)$ symmetry, this gives rise to

$$E^{(I)}(N, \omega, J, M) = \sum_{i,j} x_{ij} [\omega(\omega+2)]^i [J(J+1)]^j. \quad (3.24)$$

Introducing the quantum number $v=(N-\omega)/2$, Eq. (3.24) can be rewritten as

$$E^{(I)}(N, v, J, M) = \sum_{i,j} y_{ij} [v + \frac{1}{2}]^i [J(J+1)]^j. \quad (3.25)$$

Thus, the Dunham expansion corresponds to an expansion in terms of invariant operators of the $O(4)$ chain, and it is a special case of the more general formulation of the problem. A similar generalization of Eq. (3.17) yields

$$E^{(II)}(N, n_r, J, M) = \sum_{i,j} z_{ij} n_r^i [J(J+1)]^j. \quad (3.26)$$

C. Electromagnetic transition rates

When a dynamical symmetry is present, one can calculate in closed, analytic form all other physical properties in addition to energy levels. We discuss here briefly the calculations of electromagnetic transition rates for dipole radiation. The algebraic form of the transition operator is written in Eq. (2.22). We shall consider here only the first term in Eq. (2.22):

$$T_\mu^{(1)} = t_1^{(1)} D_\mu^{(1)}. \quad (3.27)$$

Matrix elements of this operator are obtained by inserting it between two eigenstates of H . It is convenient to separate the dependence on the magnetic quantum number M by making use of the Wigner-Eckart theorem

$$\langle \psi_{JM} | T_\mu^{(1)} | \psi'_{J'M'} \rangle = (-)^{J'-J+M'-M} \frac{\langle JMk - \kappa | J'M' \rangle}{\sqrt{2J'+1}} \langle \psi_J || T^{(1)} || \psi'_{J'} \rangle. \quad (3.28)$$

Here $\psi(\psi')$ denote the quantum numbers that specify uniquely the states, in addition to $J, M(J', M')$, and we have introduced the double bar (or reduced) matrix element.

In case I, the quantum number $\psi=N, \omega$ and we are led to calculate

$$\langle N, \omega, J || T^{(1)} || N, \omega', J' \rangle = t_1^{(1)} \langle N, \omega, J || D^{(1)} || N, \omega', J' \rangle. \quad (3.29)$$

Since the operator $D^{(1)}$ is a generator of the orthogonal group $O(4)$, the matrix elements in Eq. (3.29) have the selection rule

$$\Delta\omega = 0, \quad (3.30)$$

i. e., they cannot connect different $O(4)$ representations (bands with different vibrational quantum numbers). Furthermore, parity and angular momentum conditions imply the selection rule

$$\Delta J = \pm 1, \quad \Delta P = -. \quad (3.31)$$

Thus the only transitions to this approximation are those within the rotational levels of a band (Fig. 4). The matrix elements of the operator $D^{(1)}$ within each band can be evaluated in a straightforward way using the proper-

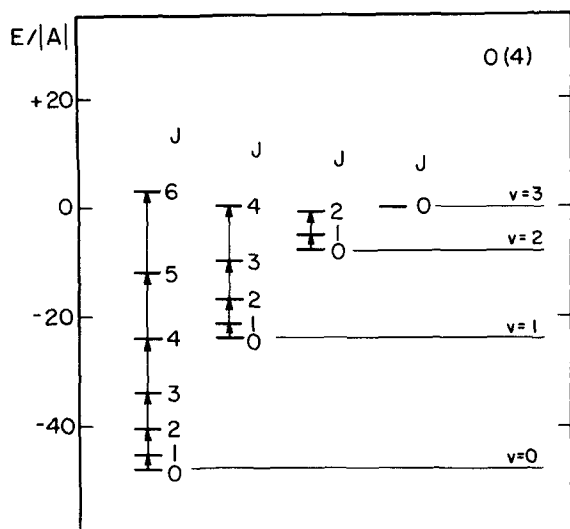


FIG. 4. An illustration of the allowed $E1$ transitions induced by the operator (3.27) in the $O(4)$ limit of the vibron model.

ties of the wave functions. For the lowest band $\omega = N$, $v = 0$ they are given by

$$\langle N, \omega, J+1 \| D^{(1)} \| N, \omega, J \rangle = \sqrt{N-J} \sqrt{N+J+2} \sqrt{J+1} . \quad (3.32)$$

For $J \ll N$, the J dependence of Eq. (3.32) is $\sqrt{J+1}$, as in the classical case.²⁰ The cutoff factor $\sqrt{N-J} \sqrt{N+J+2}$ is introduced by the termination of the bands.

An analogous calculation can be performed for the limiting case II. Here the quantum number $\psi = N$, n_r , and we are led to calculate

$$\langle N, n_r, J \| T^{(1)} \| N, n_r', J' \rangle = t_1^{(1)} \langle N, n_r, J \| D^{(1)} \| N, n_r', J' \rangle . \quad (3.33)$$

Since the operation $D^{(1)}$ contains only one π^\dagger or one $\bar{\pi}$ operator, the selection rules are now

$$\Delta n_r = \pm 1 . \quad (3.34)$$

The parity and angular momentum conditions again imply

$$\Delta J = \pm 1 , \quad \Delta P = - . \quad (3.35)$$

If each sequence of states $0^+, 1^-, 2^+, \dots$ in Fig. 3 is viewed as a band, the conditions (3.34) and (3.35) allow now for interband as well as intraband transitions (Fig. 5). The reduced matrix elements of $D^{(1)}$ can again be calculated in a straightforward way. For example, the matrix elements along the first band ($J = n_r$) are given by

$$\langle N, n_r+1, J+1 \| D^{(1)} \| N, n_r, J \rangle = \sqrt{N-J} \sqrt{2J+3} \sqrt{J+1} . \quad (3.36)$$

The dependence of these matrix elements on the quantum number J is in this case very different from $\sqrt{J+1}$. This is a consequence of the nonrigid nature of case II.

Matrix elements of higher order terms in $T_\mu^{(1)}$ and/or of the quadrupole operator $T_\mu^{(2)}$ can also be calculated if needed.

D. Other properties

Perhaps the most interesting aspect of the application of algebraic techniques to diatomic molecules is the possibility of calculating complex molecular properties. Particularly interesting is the state-to-state excitation probability $P_{\psi J M \rightarrow \psi' J' M'}$. Levine and Wulfman¹⁵ have shown how this can be done in the case of a problem described by the group $U(2)$ (one-dimensional Morse oscillator). Excitation probabilities were obtained by taking matrix elements of the operator

$$S = \exp[i(qQ_+ + q^*Q_- + \delta Q_0)] \quad (3.37)$$

between two eigenstates $|k, m\rangle$ and $|k', m'\rangle$. Since S is an element of the group $SU(2)$, this matrix element is related to the group element

$$\langle k' m' | S | k m \rangle = D_{mm'}^{(k)}(q, q^*, \delta) . \quad (3.38)$$

For $SU(2)$ these are well known (Wigner D functions). Transition probabilities are then given by

$$P_{m \rightarrow m'} = |\langle k' m' | S | k m \rangle|^2 . \quad (3.39)$$

For $U(4)$, one is led to consider the matrix elements of the operator

$$S = \exp\left(i \sum_s \alpha_s G_s\right) , \quad (3.40)$$

where G_s are the 16 generators of $U(4)$. The evaluation of the matrix elements of S requires now an explicit construction of the $U(4)$ group elements. This is a difficult but tractable mathematical problem. Moshinsky²⁴ has suggested a possible way to treat this problem. van Roosmalen²⁵ has devised another possible way and written a computer program to solve it. We are planning to use this program to study laser excitation of diatomic molecules.

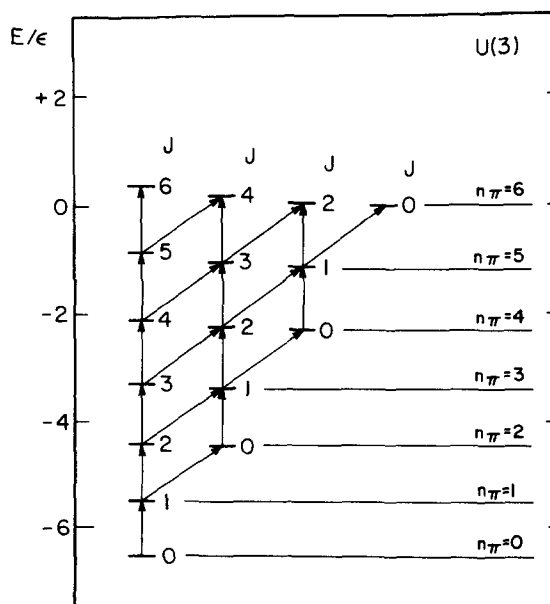


FIG. 5. An illustration of the allowed $E1$ transitions induced by the operator (3.27) in the $U(3)$ limit of the vibron model.

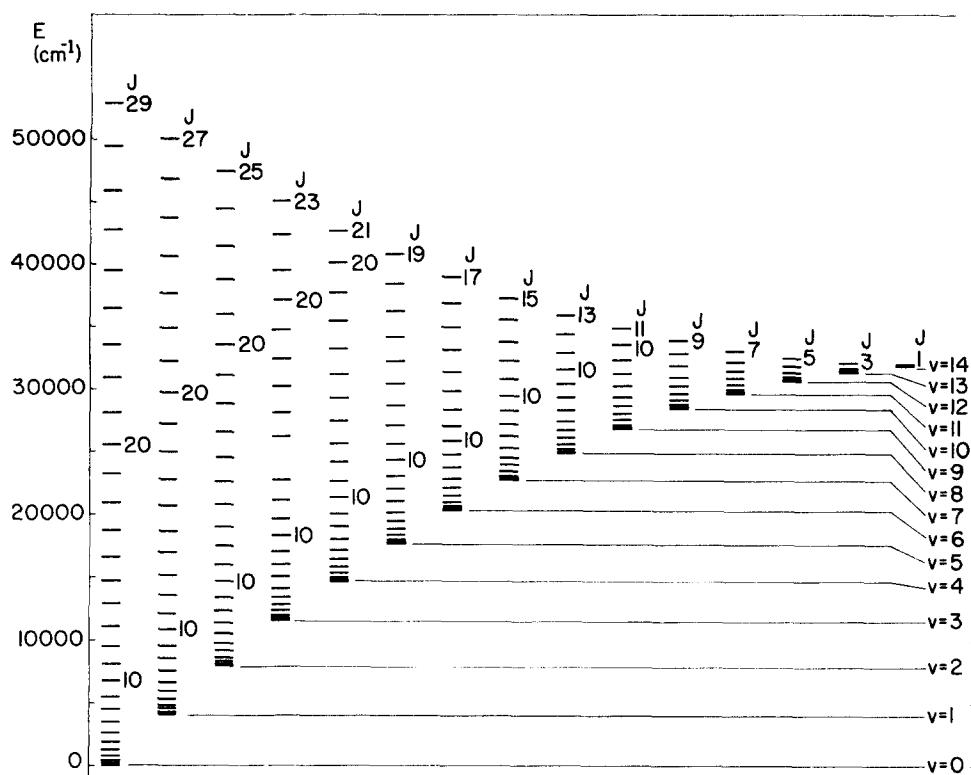


FIG. 6. A semirealistic spectrum with $O(4)$ symmetry. The energy levels are calculated using Eq. (3.8) with $N = 29$, $A = -35.421 \text{ cm}^{-1}$, $B = 60.809 \text{ cm}^{-1}$ and are counted from the lowest level $v = 0$, $J = 0$. The quantum numbers J and $v = (N - \omega)/2$ are given next to the levels.

E. Examples of dynamical symmetries

The limiting cases discussed above are interesting because they provide analytic expressions for the properties of the system that can be easily compared to experiment. Although for practical applications the limitations to two-body terms and dynamical symmetries is too restrictive and more detailed calculations must be done, it is still interesting to note that the spectra of several diatomic molecules are not far from having dynamical symmetries. Consider, for example, H_2 in its $^1\Sigma_g^+$ state. The vibrational band stops at $v_{\text{max}} = 14$. The possible values of N are $N = 28$ or $N = 29$. Assuming $N = 29$, a dynamical $O(4)$ symmetry with only quadratic terms requires $y_{10}/y_{20} = -31$. This is not far from the experimental value $y_{10}/y_{20} = -1395.21/ +117.905 = -37.28$. The spectrum corresponding to (3.8) with $-4(N+2)A = 4395.24 \text{ cm}^{-1}$ and $B = 60.809 \text{ cm}^{-1}$ is shown in Fig. 6. Comparing this spectrum with that given in Table IV of Ref. 2, one can see that the $O(4)$ symmetry with only two-body terms in H describes the observed situation reasonably well.

IV. LIMITATIONS OF THE ALGEBRAIC APPROACH

The spectrum of a realistic molecular Hamiltonian also contains a continuum part. In terms of a potential function approach, this part of the spectrum is obtained by solving the Schrödinger equation for positive energies. The algebraic approach presented in this paper is based on a compact group $U(4)$, whose unitary representations are necessarily discrete and finite-dimensional. However, as is evident from Fig. 6, the algebraic approach can account for states up to the limiting curve of dissociation.^{20,26} (Such states have energies above the dissociation energy but are quasibound by the

centrifugal barrier.) This suggests that it should prove possible to extend the algebraic approach to deal with scattering states of molecular potentials. In the case of the hydrogen atom, where a similar problem occurs, it has been found that it is possible to describe both the bound and scattering states using algebraic techniques.^{27,28} In that case, the procedure used to go from bound to scattering states is very simple, since it involves only an analytic continuation in some of the quantum numbers.²⁷ It is conceivable that a similar technique can be applied to the present case. The analytic continuation we have in mind would introduce the noncompact group $U(3,1)$. Noncompact groups have both continuous and discrete representations. In the not too distant future we also hope to present an algebraic description of scattering states. This would allow one to calculate in a simple way properties of unbound states. An interesting example here is the dissociation probability under intense laser fields.

On the practical level there are several aspects that require further attention. An obvious one is the need to go beyond the quadratic terms in Eq. (2.13) when accurate spectroscopic data is available. More work is also required on the geometric (coordinate space) interpretation of algebraic Hamiltonians.^{21,22}

V. CONCLUSIONS

We have presented here an algebraic approach to molecular rotation-vibration spectra. In this paper, we have confined ourselves to the study of diatomic molecules, in order to introduce the basic techniques (boson calculus) employed in this approach. The approach is general enough in that it can describe both rigid and nonrigid molecules. We have shown by explicit con-

struction that these two cases appear as special cases of the most general algebraic Hamiltonian H .

One of the major uses of the present approach is in the study of more complex molecules, where a potential approach is rather difficult. A second paper dealing with triatomic molecules is in preparation. A preliminary, short account of it has already appeared.¹¹ The second important use of the algebraic technique presented here is in the calculation of state-to-state excitation probabilities. Work in this direction is also in progress.

ACKNOWLEDGMENTS

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