



# Algebraic solution of the vibron model for diatomic molecules

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## Abstract

Angular momentum projected mean field theory is used to derive analytic expressions for various matrix elements in the vibron model for diatomic molecules. The results are applied in a search for a realistic description of rotation–vibration spectra in the vibron model.

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## 1. Introduction

The vibron model [1,2] offers an algebraic alternative to solving the Schrödinger equation for molecules and has been especially useful in describing complex spectra of polyatomic molecules. The basic building blocks of the model are the scalar  $s$  and vector  $p$  bosons, the latter representing the dipole degree of freedom in a molecular bond while the former is needed to generate a finite spectrum. The 16 bilinear operators  $\{b_{lm}^\dagger b_{lm}, l = 0, 1, m = -l, \dots, l\}$  close under the U(4) algebra which forms the backbone of the model (here we use the notation  $b_{00} = s, b_{1m} = p_m$ ). The U(4) algebra has two rotationally invariant subalgebra chains, namely (i)  $U(4) \supset U(3) \supset O(3) \supset O(2)$  and (ii)  $U(4) \supset O(4) \supset O(3) \supset O(2)$ . When the Hamiltonian describing the boson system is written in terms of the Casimir operators in one of the chains, the eigenvalue problem can be solved analytically. In this way, complete solutions for the U(3) and O(4) dynamical symmetry limits have been obtained [1,2]. The U(3) limit leads to a vibrational spectrum and is not of much relevance to molecules. The O(4) limit, on the other hand, leads to a spectrum similar to that of a Morse potential and hence it is appropriate for the description of rotation–vibration spectra of molecules. In its simplest form, the O(4) limit corresponds to a rigid-rotor with vanishing vibrational transitions, hence it cannot give a very accurate representation of the data. This first-order description can be improved in two ways. The first, which has been exclusively used in the literature so far, is to preserve the O(4) symmetry by adding higher order Casimir operators to the Hamiltonian. The one-body transition operator is extended similarly by including many-body terms. Although this approach has the advantage that analytic expressions for energies (such as the Dunham expansion) and transitions can be readily given, this comes at the cost of introducing many more parameters in the model. In the second method, one breaks the O(4) symmetry by adding terms from the U(3) chain to the Hamiltonian. A general study of symmetry breaking effects requires numerical diagonalization of the Hamiltonian which may explain why it has been neglected. (In contrast, symmetry breaking has been the main approach in realistic applications of the interacting boson model (IBM) in nuclear physics [3].)

The purpose of this Letter is to apply angular momentum projected mean field theory techniques to the vibron model for diatomic molecules and derive analytic solutions for general Hamiltonians. The results are used in a study of the symmetry breaking effects to assess whether it provides a viable alternative to the symmetry preserving approach.

## 2. Angular momentum projected mean field theory

Mean field techniques have been extensively used in the vibron model to discuss its geometrical content and to provide a link with the more conventional models based on geometrical variables [4–10]. The starting point of mean field calculations is the variational state for the system which, choosing the intrinsic (molecular) axis along the  $z$  direction, can be written as a boson condensate,

$$|N, r\rangle = (N!)^{-1/2} (b^\dagger)^N |0\rangle, \quad b^\dagger = (1 + r^2)^{-1/2} (s^\dagger + r p_0^\dagger). \quad (1)$$

Here  $N$  is the number of bosons and  $r$  is a variational parameter determined from the minimum of the energy surface,  $E(r) = \langle N, r | H | N, r \rangle$ , for a given Hamiltonian  $H$ . Because the condensate (1) breaks the rotational invariance, matrix elements obtained in the intrinsic frame are correct to leading order in  $1/N$ , and hence can only provide a qualitative description. For comparison with experimental data, one needs more accurate results which can be achieved by performing angular momentum projection before variation. Since variation after projection with a complete set of states is equivalent to solving the Schrödinger equation, this approach can provide analytical solutions for general vibron model Hamiltonians. Such a program has been carried out in the IBM [11] and was shown to lead to a  $1/N$  expansion for all matrix elements.

The starting point of the  $1/N$  expansion calculations is the evaluation of the normalization integral for the condensate (1) with angular momentum projection

$$\mathcal{N}(N, L) = \langle N, r | P_{00}^L | N, r \rangle, \quad (2)$$

where  $P_{00}^L$  is the projection operator [12]. Using boson calculus and angular momentum algebra techniques [11], one obtains for the matrix element (2)

$$\mathcal{N}(N, L) = \frac{1}{2}(2L + 1) \int_0^\pi d\beta \sin \beta d_{00}^L(\beta) \left( \frac{1 + r^2 \cos \beta}{1 + r^2} \right)^N. \quad (3)$$

The integral in Eq. (3) has been evaluated in closed form in terms of the hypergeometric function  ${}_2F_1$  as [13] (a second term, which is completely negligible in practice, is ignored here)

$$\mathcal{N}(N, L) = \frac{2L + 1}{a(N + 1)} {}_2F_1(-L, L + 1; N + 2; 1/a), \quad (4)$$

where

$$a = 2r^2/(1 + r^2), \quad (5)$$

represents the ‘average angular momentum squared’ carried by an intrinsic boson and provides a more convenient parametrization of expressions than  $r$ . Expanding  ${}_2F_1$  in  $1/N$  and  $\bar{L} = L(L + 1)$ , one finally obtains the desired form for the normalization

$$\mathcal{N}(N, L) = \frac{2L + 1}{aN} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!(aN)^n} \sum_{m=0}^n \alpha_{nm} \bar{L}^m. \quad (6)$$

The coefficients  $\alpha_{nm}$  in (6) are polynomials in  $a$ , and the first few are given by

$$\begin{aligned} \alpha_{nn} &= 1, & \alpha_{n0} &= n!a^n, & \alpha_{21} &= 6a - 2, & \alpha_{32} &= 18a - 8, & \alpha_{31} &= 6(7a^2 - 6a + 2), \\ \alpha_{43} &= 40a - 20, & \alpha_{42} &= 4(75a^2 - 80a + 27), & \alpha_{41} &= 24(15a^3 - 25a^2 + 20a - 6). \end{aligned}$$

The condensate (1) generates the ground ( $v=0$ ) band. In mean field theory, the other vibrational bands  $|N, v\rangle$  are obtained by replacing the intrinsic bosons  $b$  with the orthogonal ones  $b'$ ,

$$|N, v\rangle = [(N-v)!v!]^{-1/2} (b^\dagger)^{N-v} (b')^v |0\rangle, \quad b'^\dagger = (1+r^2)^{-1/2} (rs^\dagger - p_0^\dagger). \quad (7)$$

Although these bands are orthogonal by construction, this property is lost after angular momentum projection, and must be restored. In this process, we use the O(4) states as a guide and follow a procedure similar to the Schmidt method. For example, the first vibrational band is modified to

$$|N, v=1\rangle = [(N-1)!]^{-1/2} \left[ (b^\dagger)^{N-1} b'^\dagger + \xi (b^\dagger)^{N-2} p_1^\dagger p_{-1}^\dagger \right] |0\rangle. \quad (8)$$

The coefficient  $\xi$  is determined from the condition  $\langle N, v=1 | P_{00}^L | N, v=0 \rangle = 0$  as

$$\xi = \left( \frac{2-a}{a} \right)^{1/2} \left\{ 1 + \frac{1-a}{aN} \sum_m \left[ 2 \left( \frac{2-a}{aN} \right)^m - (1 + \delta_{m1}) \left( \frac{\bar{L}}{aN} \right)^m \right] \right\}, \quad (9)$$

where only the leading contribution to powers of  $\bar{L}$  is shown for compactness. The O(4) limit ( $r=a=1$ ), provides an important check on the calculations. For  $a=1$ , Eq. (9) gives  $\xi=1$  in agreement with the group theoretical result [2].

The simplest way to break the O(4) limit is to include a  $p$  boson energy term  $\epsilon \hat{n}_p$  in the O(4) Hamiltonian,

$$H = -\kappa \hat{D} \cdot \hat{D} + \kappa' \hat{L} \cdot \hat{L} + \epsilon \hat{n}_p. \quad (10)$$

The dipole, angular momentum and the number operators in (10) are defined as

$$\hat{D}_\mu = [s^\dagger \tilde{p} + p^\dagger \tilde{s}]_\mu^{(1)}, \quad \hat{L}_\mu = -\sqrt{2} [p^\dagger \tilde{p}]_\mu^{(1)}, \quad \hat{n}_p = \sum_\mu p_\mu^\dagger p_\mu, \quad (11)$$

where brackets denote tensor coupling and tilde  $\tilde{b}_{lm} = (-1)^m b_{l-m}$ . The expectation value of  $\hat{L} \cdot \hat{L}$  with projection gives  $L(L+1)$  as expected from rotational invariance. Since it does not play any role in the dynamics of the system, it will not be discussed further. (In applications, it can be restored by adding  $\kappa' \bar{L}$  to the final energy expressions.) For the one-body term, one needs to evaluate

$$\langle \hat{n}_p \rangle_L = \langle N, r | \hat{n}_p P_{00}^L | N, r \rangle / \mathcal{N}_g(N, L). \quad (12)$$

Using boson calculus, this can be reduced to the form

$$\langle \hat{n}_p \rangle_L = \frac{aN}{2F(N, L)} \sum_I \langle L0100 | I0 \rangle^2 F(N-1, I), \quad (13)$$

where we have introduced  $\mathcal{N}_g(N, L) = (2L+1)F(N, L)/a$  to simplify the expression. The angular momentum sums involving the Clebsch–Gordon coefficient in (13) can be calculated using the techniques described in Ref. [11]. Note that Eq. (13) basically involves the quotient of the normalization (6) with different arguments. This form is typical of all other matrix elements and underscores the importance of the exact evaluation of the normalization integral. In principle,  $\langle \hat{n}_p \rangle_L$  can be calculated to any desired accuracy in powers of  $1/N$ , though a hand calculation becomes a rather arduous task beyond the first few powers. Fortunately, Eq. (13) can be

easily adapted to computer algebra which can do the manipulations much faster and more accurately. Here we present a Mathematica [14] evaluation of (13) to order  $1/N^6$ ,

$$\begin{aligned} \langle \hat{n}_p \rangle_L = \frac{1}{2} aN \left\{ 1 - \frac{2-a}{aN} + \frac{\bar{L}}{(aN)^2} (2-a) \left[ 1 + 2(1-a) \left( \frac{1}{aN} + \frac{3-2a}{(aN)^2} \right) \right. \right. \\ \left. \left. + \frac{12-15a+4a^2}{(aN)^3} + \frac{60-108a+57a^2-8a^3}{(aN)^4} \right] \right\} \\ + \frac{\bar{L}^2}{(aN)^4} (2-a)(1-a) \left( 1 + \frac{8-7a}{aN} + \frac{56-88a+33a^2}{(aN)^2} \right) + \frac{\bar{L}^3}{(aN)^6} 2(2-a)(1-a)^2 \left. \right\}. \end{aligned} \quad (14)$$

For  $a=1$ , Eq. (14) reproduces the O(4) limit result [2]  $\langle \hat{n}_p \rangle_L = \frac{1}{2}(N-1 + \bar{L}/N)$ . Note that the order  $1/N^6$  is needed to calculate the coefficient of the  $\bar{L}^3$  term but otherwise leads to unnecessary accuracy for the other powers of  $\bar{L}$  (e.g. better than 1 part per million for  $\bar{L}$ ). A more economical presentation of the results without undue loss of accuracy can be achieved by using the layers concept [11]. For an  $n$ th layer calculation, where  $n$  corresponds to the maximum power of  $\bar{L}/N^2$  in the expansion, the number of  $1/N$  terms for  $\bar{L}^m$  is reduced to  $k = n + 1 - m$  from the  $2k - 1$  terms in the complete expansion to order  $1/N^{2n}$ . Thus restricting the expansion to the third layer, we obtain for the expectation value of the dipole interaction

$$\begin{aligned} \langle \hat{D} \cdot \hat{D} \rangle_L = aN^2 \left\{ 2-a + \frac{1+2a-a^2}{aN} - \frac{\bar{L}}{(aN)^2} (2-a) \left[ 2a-1 - 2(1-a)^2 \left( \frac{1}{aN} + \frac{3-2a}{(aN)^2} \right) \right] \right. \\ \left. - \frac{\bar{L}^2}{(aN)^4} (2-a)(1-a)^2 \left( 1 + \frac{8-7a}{aN} \right) + \frac{\bar{L}^3}{(aN)^6} 2(2-a)(1-a)^3 \right\}. \end{aligned} \quad (15)$$

For  $a=1$ , Eq. (15) reduces to the O(4) result,  $\langle \hat{D} \cdot \hat{D} \rangle_L = N^2 + 2N - \bar{L}$ . Introducing  $\eta = \epsilon/4N\kappa$ , the ground-band energy for the Hamiltonian (10) can be written in a compact form suitable for variation

$$\begin{aligned} E(a, L) = \kappa N^2 \left\{ a(a-2+2\eta) + \frac{1}{N} [a^2 - 2a - 1 + 2\eta(a-2)] \right. \\ \left. + \frac{\bar{L}}{N^2} \frac{2-a}{a} \left[ 2a-1+2\eta + 2(1-a)(a-1+2\eta) \left( \frac{1}{aN} + \frac{3-2a}{(aN)^2} \right) \right] \right. \\ \left. - \frac{\bar{L}^2}{N^4} \frac{2-a}{a^3} (1-a)(a-1+2\eta) \left( 1 + \frac{8-7a}{aN} \right) + \frac{\bar{L}^3}{N^6} \frac{2-a}{a^5} 2(1-a)^2(a-1+2\eta) \right\}. \end{aligned} \quad (16)$$

Setting the derivative of  $E(a, L)$  to zero, one obtains a complicated equation for  $a$ . This can be solved, in the spirit of the  $1/N$  expansion, by substituting the Ansatz  $a = \sum_{nm} a_{nm} (\bar{L}/N^2)^n / N^m$  in the derivative and setting each order to zero. The resulting set of linear equations for  $a_{nm}$  can be easily solved and one obtains for  $a$  to the second layer

$$a = 1 - \eta + \frac{\bar{L}}{N^2} \left( \frac{\eta}{1-\eta} \right)^2 \left( 1 + \frac{2}{N} \frac{1+\eta}{1-\eta} \right) - \frac{\bar{L}^2}{N^4} \frac{\eta^3(3-\eta)}{(1-\eta)^5}. \quad (17)$$

The calculation of  $a$  to the second layer is sufficient because due to the Hartree–Bose condition, each layer in  $a$  contributes to the next one in  $E$ . Finally, substituting (17) in (16), we obtain an expression for the ground-band energy directly in terms of the Hamiltonian parameters

$$E(v=0, L) = \kappa N^2 \left[ -(1-\eta)^2 - \frac{1}{N}(2+2\eta+\eta^2) + \frac{\bar{L}}{N^2} \frac{1+\eta}{1-\eta} \left( 1 + \frac{1}{N} \frac{2\eta^2}{1-\eta} + \frac{1}{N^2} \frac{2\eta^2(1+2\eta)}{(1-\eta)^2} \right) - \frac{\bar{L}^2}{N^4} \frac{\eta^2}{(1-\eta)^4} \left( 1 + \frac{1}{N} \frac{1+7\eta+4\eta^2-4\eta^3}{1-\eta} \right) + \frac{\bar{L}^3}{N^6} \frac{2\eta^3(1+\eta)}{(1-\eta)^7} \right]. \quad (18)$$

Energy expressions for other vibrational bands can be calculated following similar steps. We present here the result for the  $v=1$  band to demonstrate the effect of symmetry breaking on the excited bands

$$E(1, L) = E(0, L) + \kappa N \left[ 4 - 2\eta_2 + \frac{\bar{L}}{N^2} \frac{4\eta}{(1-\eta)^2} \left( 2 + \eta + \eta^2 + \frac{2}{N} \frac{2+4\eta+3\eta^2+\eta^3}{1-\eta} \right) - \frac{\bar{L}^2}{N^4} \frac{2\eta^2}{(1-\eta)^5} (9 + 7\eta + 4\eta^2 - 16\eta^3 + 4\eta^4) \right]. \quad (19)$$

For  $\eta=0$ , one obtains  $4\kappa N$  for the excitation energy consistent with the O(4) result.

We next discuss electric dipole transitions which provide sensitive tests for the wavefunctions. For the ground-band, one needs to evaluate

$$\langle 0, L' | \hat{D} | 0, L \rangle = N [a(2-a)]^{1/2} (2L+1)^{1/2} \langle 10L0 | L'0 \rangle \frac{F(N-1, L) + F(N-1, L')}{[F(N, L)F(N, L')]^{1/2}}. \quad (20)$$

Since intensity measurements are not as accurate as energy levels, a first layer calculation is sufficient in this case. For  $L'=L+1$  we obtain

$$\langle 0, L+1 | \hat{D} | 0, L \rangle = N(L+1)^{1/2} (1-q^2)^{1/2} \left( 1 + \frac{1}{N} - \frac{L(L+2)}{N^2} \frac{1-2\eta-\eta^2}{(1-\eta)^3(1+\eta)} \right). \quad (21)$$

A similar calculation for the  $\Delta v=1$  transition gives

$$\langle 1, L+1 | \hat{D} | 0, L \rangle = [N(L+1)]^{1/2} \eta \left( 1 - \frac{2L+1+\eta}{2N(1-\eta)} \right). \quad (22)$$

Both equations agree with the O(4) results when  $\eta=0$ . In addition, we have checked the analytic expressions presented here against numerical results in cases when  $\eta \neq 0$ .

### 3. Applications to molecular spectra

We use the  $1/N$  formulae to study the effects of symmetry breaking in various quantities and contrast them with the available data on halides. We limit ourselves to the leading order terms in  $1/N$  which is sufficient for a qualitative discussion and has the advantage that the  $N$  dependence can be factored out from the expressions. Further, we use ratios thereby eliminating  $\kappa$  which is a scale parameter and best determined from the first vibrational energy  $\Delta E = E(1, 0) - E(0, 0)$ . We denote Eq. (18) as  $E(0, L) = \sum_n C_n \bar{L}^n$  and the difference between the  $C_1$  coefficients of  $v=1$  and 0 bands as  $\Delta C_1$ . Fig. 1 shows four such ratios which are to be compared with the data shown in Table 1. We comment on their salient features below.

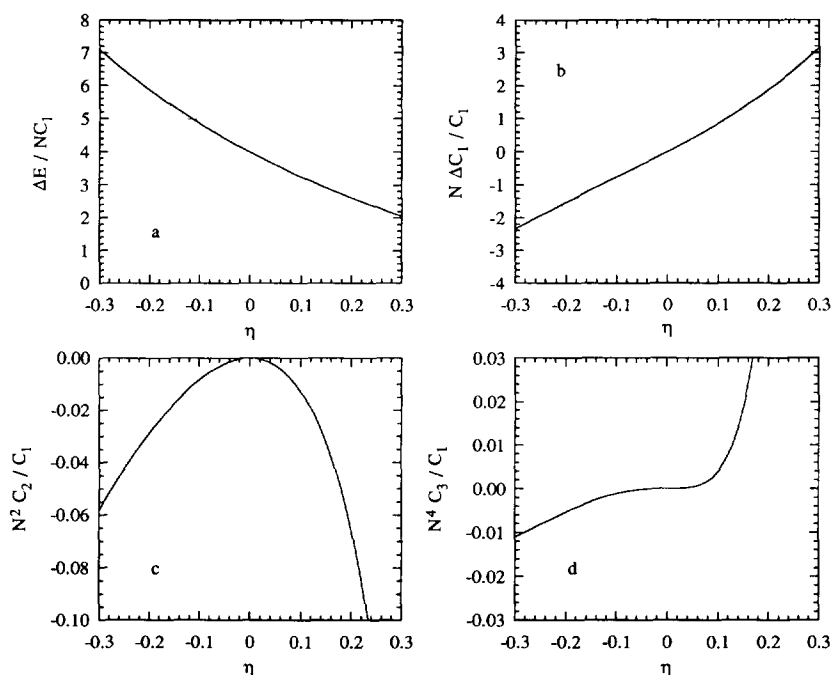


Fig. 1. The effect of the one-body breaking term ( $\eta = \epsilon / 4N\kappa$ ) on various energy ratios.

(a)  $\Delta E / NC_1$ ; this ratio is 4 in the O(4) limit. By choosing a negative  $\eta$  around  $-0.1$ , one can describe the experimental moments of inertia without the  $\kappa'$  term in (10).

(b)  $N\Delta C_1 / C_1$ ; in the O(4) limit, all the bands have the same moment of inertia contrary to observations. Choosing  $\eta \sim -0.2$  is seen to explain the reduction in  $C_1$  values.

(c)  $N^2 C_2 / C_1$ ; for  $\eta < 0$ , symmetry breaking accounts for a fraction of the  $C_2$  values.

(d)  $N^4 C_3 / C_1$ ; both sign and magnitude of  $C_3$  are not right for  $\eta < 0$ .

Since the importance of the quantities decreases from (a)–(d), the preceding analysis suggests that a negative  $\epsilon$  is to be preferred for breaking of the O(4) symmetry. The discrepancies in  $C_2$  and  $C_3$  may be resolved by including higher order terms in the Hamiltonian which will be pursued in a longer paper.

Experimentally, the  $\Delta v = 1$  dipole transitions are an order of magnitude smaller than those of  $\Delta v = 0$ . From Eqs. (21) and (22) this ratio is roughly given by  $\eta / \sqrt{N}$  which is clearly not large enough for the  $\eta$  values indicated above. This again suggests the need for higher order terms in the transition operator [16].

Table 1

Experimental values for halides [15] of the ratios considered in Fig. 1. The O(4) values are shown on the bottom row for reference.

Molecule	$N$	$\Delta E / NC_1$	$N\Delta C_1 / C_1$	$N^2 C_2 / C_1$	$N^4 C_3 / C_1$
HF	44	4.38	-1.65	-0.20	0.029
HCl	55	5.03	-1.60	-0.15	
HBr	57	5.38	-1.58	-0.13	0.009
O(4)		4.00	0	0	0

#### 4. Conclusions

In this Letter, we have developed analytic  $1/N$  expansion solutions for the vibron model of diatomic molecules and applied the results in a simple study of symmetry breaking effects. We have shown that the  $O(4)$  results can be improved by adding the one-body term in the Hamiltonian, though higher-order terms are needed for a more accurate representation of data.

The formalism provides wavefunctions for general Hamiltonians which could be used in electron scattering and other molecular collision processes. Besides their intrinsic value, the results for diatomic molecules provide a basis for  $1/N$  calculations in polyatomic molecules which will be pursued in future articles.

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