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Mean-field approach to the algebraic treatment of molecules: Linear molecules

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We study recently proposed algebraic models [F. Iachello, Chem. Phys. Lett. **78**, 581 (1981); F. Iachello and R. D. Levine, J. Chem. Phys. **77**, 3046 (1982); F. Iachello, S. Oss, and R. Lemus, J. Mol. Spectrosc. **146**, 56 (1991); F. Iachello and S. Oss, *ibid.* **149**, 132 (1991)] for diatomic and linear polyatomic molecules in the mean-field approximation. In this approach, we recover the harmonic molecular spectra efficiently and accurately and, more importantly, we are able to explore the geometrical meaning of boson operators and to suggest boson Hamiltonians that have closer links to molecular geometries.

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I. INTRODUCTION

Recently Iachello and co-workers [1] have demonstrated the great power of algebraic approaches to molecular dynamics. These methods have been applied with success to the spectra and transition intensities in diatomic molecules [2], bent and linear triatomic molecules [3, 4], linear four-atom molecules [5], and even complex polyatomic molecules [6]. The algebraic method has been shown to be a rich starting point for studies of electron scattering from molecules [7, 8], and promises to be a fertile starting point for other reaction studies [9]. The principle disadvantage of the vibron model, as this approach is called, is that the molecular dynamics is expressed in terms of boson operators that are not easily interpreted in terms of the atomic position coordinates of traditional molecular physics. The standard way of extracting geometric meaning from boson models is through the use of coherent-state mean-field techniques [10–20].

In this paper we show that by applying mean-field methods to the algebraic description, we not only greatly simplify the algebra, but also make a connection between the algebraic degrees of freedom and the coordinate degrees of freedom. The mean-field approximation is basically an expansion in $1/N$ and is particularly appropriate in a discussion of the algebraic treatment of molecular dynamics since the number of bosons (N) is normally quite large. In this limit we have both the simplification of the mean-field approximation and the fact that the operators approach classical values. It is these two features that we exploit.

This paper is meant to be an introduction to the mean-field approximation (MFA) for algebraic descriptions of molecules. As such the paper is partly pedagogic. We will show how the MFA comes out of the vibron model and how the correct dynamical and zero modes emerge. We will show how the molecular equilibrium shape (in the intrinsic frame) comes out and how it depends on the input parameters. We will stress the connection between the equilibrium shape, the dynamical modes, and the zero modes. We will compare our results with those obtained from the full vibron model. We will see that the spectra are not quite so accurately given as in the full model, since we omit both $1/N$ corrections and anharmonicities. These can be included, but that is not the point of the approach. For many purposes, such as electron scattering, reactions, and the description of complex molecules, the accuracy we obtain is sufficient, and the simplicity of the description a boon. It is that description and its direct contact to molecular shape that is the strongest appeal of the method.

In Sec. II we introduce the method in a "toy" model based on the vibron model for the group U(2). In Sec. III we treat a diatomic molecule using group U(4). In Sec. IV we discuss the MFA treatment of linear triatomic molecules, that are described in the vibron model with U(4)×U(4). Here we compare our results for energies and discuss the use of the MFA for transition intensities. In Sec. V we treat linear four-atom molecules. In Sec. VI we present some discussion, a summary, and a plan for further work, which includes the treatment of bent molecules. In Appendix A we show an equivalent formulation in terms of complex classical variables [random-phase approximation (RPA)]. In Appendix B we discuss the bond length of a diatomic molecule in the MFA of the vibron model.

II. U(2) VIBRON MODEL

The U(2) vibron model can be used to describe a single vibrational degree of freedom [16, 15]. The u(2) algebra is expressed in terms of two bosons, σ and τ, with the usual commutation relations. The algebra is generated by the number operator

$$N = \tau^\dagger \tau + \sigma^\dagger \sigma, \tag{1}$$

and a set of operators that satisfy the commutation relations of angular momentum, SU(2),

$$J_x = (\sigma^\dagger \sigma - \tau^\dagger \tau)/2, \tag{2}$$

$$J_y = i(\tau^\dagger \sigma - \sigma^\dagger \tau)/2, \tag{3}$$

$$J_z = -(\tau^\dagger \sigma + \sigma^\dagger \tau)/2. \tag{4}$$

A simple "vibron" model is given by the pairing Hamiltonian

$$H = AP_2 = \frac{A}{4}(\tau^\dagger\tau^\dagger - \sigma^\dagger\sigma^\dagger)(\tau\tau - \sigma\sigma), \tag{5}$$

with $A > 0$. This Hamiltonian clearly conserves total boson number, N. In the symmetric representation, the eigenstates of H are $|[N]v\rangle$ with $v = 0, 1, \ldots, N$, where v is the vibrational quantum number and the system has $N + 1$ vibrational states. Equivalently, these states can be written with the SU(2) labels in the form $|JM\rangle$ with $J = N/2$ and $M = v - N/2$.

Using group theory, we obtain the energy eigenvalues of H as

$$E(v) = Av(N - v). \tag{6}$$

When $v \ll N$, (6) reduces to a harmonic spectrum $E(v) \approx \omega v$ with frequency $\omega = AN$. This approximation is good if N is very large, and v is far from N. We now show how one can obtain the same large N result using the MFA. In this method one takes as variational ansatz a mean field or boson condensate state. In this state there are N identical bosons which are formed from a particular linear combination of the dynamical bosons. The correct combination is found variationally. The state associated with this combination is then treated as a classical mean field, the condensate, and we study quantum fluctuations around it. Because the mean field is a variational solution to the dynamics, the fluctuations must be orthogonal to that field. The variational state can be written as

$$|c\rangle = |[N]r\rangle = \frac{1}{\sqrt{N!}}c^{\dagger N}|0\rangle, \tag{7}$$

with the condensate boson given by

$$c^\dagger = \frac{1}{\sqrt{1+r^2}}(\tau^\dagger + r\sigma^\dagger), \tag{8}$$

where r is a variational parameter. The expectation value of H in the condensate is

$$E(r) = \frac{A}{4}\left(\frac{1-r^2}{1+r^2}\right)^2, \tag{9}$$

and is minimal at $r = \pm 1$. The fact that we have two minima reflects that states with $\pm M$ are degenerate. For simplicity we concentrate on the minimum $r = 1$, but a similar analysis can be made for the case $r = -1$. The real eigenstates are the symmetric and antisymmetric combination of the states built on either minimum [13].

The condensate boson becomes $c^\dagger = \frac{1}{\sqrt{2}}(\tau^\dagger + \sigma^\dagger)$. The fluctuations are then generated by the orthogonal *fluctuation boson* (FB) which can be taken to be $a^\dagger = \frac{1}{\sqrt{2}}(-\tau^\dagger + \sigma^\dagger)$. We rewrite the Hamiltonian in terms of the c and a bosons. The condensate bosons c and $c^\dagger$ can be replaced by their classical mean-field value $\sqrt{N}$. We then get to leading order in the FB

$$H \approx ANa^\dagger a. \tag{10}$$

This is a harmonic-oscillator Hamiltonian with frequency $\omega = AN$, and is completely equivalent to the full U(2) solution in the large-N limit. In the MFA the vibrational states are given by the normal mode harmonic states

$$|v\rangle = \frac{a^{\dagger v}}{\sqrt{v!}}|0\rangle. \tag{11}$$

These replace the exact quantum states $|JM\rangle$.

We can also use the MFA to calculate transition matrix elements. Let us take the transition operator in this toy model to be a function of J_y in the vibron model. We take the operator to be $e^{i\theta J_y}$. Then a transition matrix element between the ground state $M = -N/2$ and some excited state $M' = n - N/2$ is given by

$$T_{n0} = \langle JM'|\exp(-i\theta J_y)|JM\rangle = d^J_{M'M}(\theta)$$
$$= \sqrt{\frac{N!}{n!(N-n)!}}\left(\cos\frac{\theta}{2}\right)^{N-n}\left(-\sin\frac{\theta}{2}\right)^n. \tag{12}$$

In the MFA, $J_y = \frac{i}{2}\sqrt{N}(a - a^\dagger)$ and so the transition matrix element is simply

$$T_{n0} = \langle n|\exp\left(\frac{\theta}{2}\sqrt{N}(a - a^\dagger)\right)|0\rangle$$
$$= e^{-\frac{\theta^2 N}{8}}(-1)^n\left(\frac{\theta}{2}\right)^n\sqrt{\frac{N^n}{n!}}. \tag{13}$$

It can be seen that when $\theta < 1$ and $n \ll N$, (13) is a good approximation to (12).

Hence calculation in terms of normal mode states is accurate at large N. In the MFA we replace the condensate boson by $\sqrt{N}$ and expand in the FB's, a and $a^\dagger$. The u(2) algebra then collapses into an algebra generated by $a^\dagger$, a, $a^\dagger a$, and I (unit operator). This new algebra is the Heisenberg algebra h_4 and our prescription describes the process of contraction of the Lie algebra u(2) to h_4. Contractions of Lie algebras are discussed in detail by Gilmore [21] and have been used in a different context by Alhassid and Levine [22].

III. U(4) VIBRON MODEL

In the vibron model the appropriate group for a diatomic molecule is group U(4). It is realized in terms of four bosons, p_x, p_y, p_z, and s, where the three components of **p** form a vector. A general Hamiltonian that conserves angular momentum and is at most quadratic in the generators of the u(4) algebra has two possible group chains where we can solve for the eigenvalues anaytically [1]. One is the so-called U(3) limit with the group chain U(4)⊃U(3)⊃O(3). This describes a harmonic oscillator. The other one is the O(4) limit with the group chain U(4)⊃O(4)⊃O(3) and can be shown to correspond to the Morse potential [1]. Most diatomic molecules are well described by the O(4) limit and hereafter we shall concentrate on this case.

We express the Hamiltonian in terms of the Casimir invariants in the group chain U(4)⊃O(4)⊃O(3) by

$$H = -AC_2(\mathrm{O}(4)) + BC_2(\mathrm{O}(3)), \tag{14}$$

where, of course, $C_2(\mathrm{O}(3))$ is the square of the angular momentum. In terms of the bosons the angular momentum is given by $\mathbf{L} = -i\mathbf{p}^\dagger \times \mathbf{p}$. The Casimir invariant for O(4), $C_2(\mathrm{O}(4))$, is given in terms of the dipole operator **D** and the angular momentum operator by

$$C_2(O(4)) = \mathbf{D}\cdot\mathbf{D} + \mathbf{L}\cdot\mathbf{L}, \tag{15}$$

where

$$\mathbf{D} = s^\dagger \mathbf{p} + \mathbf{p}^\dagger s. \tag{16}$$

The Hamiltonian commutes with the total boson number operator $\hat{N} = s^\dagger s + \mathbf{p}^\dagger \cdot \mathbf{p}$, which is the Casimir invariant of group U(4).

Using group theoretical methods we find for the eigenvalues of H

$$E(v, L) = -A\sigma(\sigma + 2) + BL(L + 1), \tag{17}$$

where σ can be written in terms of the vibrational quantum number v as $\sigma = N - 2v$. In the large-N limit, ($N \gg 1$, $v \ll N$), we have

$$E \approx -A(N^2 + 2N) + 4ANv + BL(L + 1). \tag{18}$$

Once again this is a harmonic spectrum with $\omega = +4AN$.

To solve the problem in the MFA we must find the optimal boson condensate. As in the U(2) case, we parametrize the condensate boson as

$$b_c = \frac{1}{\sqrt{1 + r^2}}(s + \mathbf{r}\cdot\mathbf{p}) \tag{19}$$

and write the mean-field state as

$$|N, \mathbf{r}\rangle = \frac{1}{\sqrt{N!}}(b_c^\dagger)^N |0\rangle, \tag{20}$$

where $\mathbf{r}$ is the variational parameter. Minimizing H in the condensate state gives $r = 1$, but does not fix the direction of $\mathbf{r}$. We are free to pick that direction, so we take $\mathbf{r} = \hat{\mathbf{z}}$. This breaking of the rotational invariance of the Hamiltonian by the intrinsic state is familiar in many branches of physics. For our case it corresponds to the fact that the dipolar molecule has an intrinsic orientation, which we take here to be along z. The optimal condensate boson is then

$$b_c^\dagger = \frac{1}{\sqrt{2}}(s^\dagger + p_z^\dagger). \tag{21}$$

The orthogonal FB's are then $b_z^\dagger = \frac{1}{\sqrt{2}}(-s^\dagger + p_z^\dagger)$, $b_x^\dagger = p_x^\dagger$ and $b_y^\dagger = p_y^\dagger$. We rewrite the Hamiltonian in terms of the condensate and fluctuation bosons. We then make the following replacement as often as possible:

$$b_c^\dagger b_c \to N - b_z^\dagger b_z - b_x^\dagger b_x - b_y^\dagger b_y. \tag{22}$$

The remaining terms that still contain condensate bosons are then replaced by $\sqrt{N}$,

$$b_c^\dagger \to \sqrt{N}, \quad b_c \to \sqrt{N}. \tag{23}$$

These rules are an algebraic equivalent of deriving the standard RPA Hamiltonian in the large-N limit [17].

Neglecting terms which contain more than two FB's as well as constant terms, we obtain for the Hamiltonian in the MFA

$$H \approx 4ANb_z^\dagger b_z - \frac{BN}{2}[(b_x^\dagger - b_x)^2 + (b_y^\dagger - b_y)^2]. \tag{24}$$

This shows that we have a harmonic term in the b_z boson and zero modes in the b_x and b_y bosons. If we replace the boson operators by the standard combination of coordinates and momenta, the last two terms are clearly pure momentum operators. They can be shown to correspond to the mean-field limit of L_x^2 and L_y^2. The angular momentum term [the second term in (24)] has expectation value proportional to N in the condensate for any $\mathbf{r}$, and in the large-N limit does not contribute to the energy of the condensate. It contributes only to the kinetic energy of the molecule. Its energy is in the two zero modes (Goldstone modes) associated with the breaking of rotational invariance. We note that the MFA with the prescription given in (22) and (23) gives the correct number of modes, one stretching vibration and two rotational zero modes. The four original bosons lead to only three modes because the condensate boson has been promoted to a classical variable and given its classical expectation value [18]. In Appendix A we show that these same results can be obtained by using the RPA.

The simple condensate with $r = 1$ presented here reflects our choice of a Hamiltonian in the U(4)⊃O(4)⊃O(3) group chain. An alternate choice would be the dynamical symmetry group chain U(4)⊃U(3)⊃O(3). The Casimir invariant of U(3), $C_2(\mathrm{U}(3))$, equals $\hat{N}_p(\hat{N}_p + 2)$. Where $\hat{N}_p$ is the number operator of p bosons. A Hamiltonian with $C_2(\mathrm{U}(3))$ alone would lead, in the MFA, to $r = 0$. Clearly a Hamiltonian containing terms in both $C_2(\mathrm{O}(4))$ and $C_2(\mathrm{U}(3))$ would, in the MFA, lead to some r between 0 and 1. The eigenvalues of such a Hamiltonian cannot be derived in closed form using group theoretic methods, but are easily found in the MFA. Since most diatomic molecules, although close to the O(4) limit, do not have the exact dynamical symmetry, realistic Hamiltonians can have minima at r slightly different from 1. The ease of solution in the MFA of the mixed Hamiltonian should make this physically attractive solution more accessible.

To connect the algebraic degrees of freedom studied in the MFA with the coordinate degrees of freedom of the diatomic molecule, we need an expression for the expectation value of the bond length **B**. We take

$$\langle N, \mathbf{r}|\mathbf{B}|N, \mathbf{r}\rangle = \sqrt{\frac{\hbar N}{m\omega}}\frac{\mathbf{r}}{\sqrt{1 + r^2}}, \tag{25}$$

where m is the reduced mass of the atomic pair and ω is the stretching frequency. A discussion of this formula is given in Appendix B. In Table I we show some results of formula (25) for the expected value of the bond length compared with known experimental values. To use (25) we take the reduced masses and stretching frequencies from experiment and we take r and N from the vibron model, where they are determined by fitting the spectra [3, 4]. We see in Table I that the results are surprisingly

TABLE I. Bond lengths of diatomic molecules.

Molecule	r_e (Å)	B (Å)	Error
CO	1.06	1.07	0.9%
CN	1.16	1.10	5.1%
CS	1.55	1.36	12.3%
NO	1.15	1.00	12.8%
N_2	1.09	1.02	6.4%
HS	1.35	1.34	0.74%
LiF	1.56	1.59	1.9%
HF	0.917	1.11	21.0%
HCl	1.27	1.43	12.6%
K_2	3.92	3.90	0.51%

good considering that this harmonic mean field estimate is only correct to order $\frac{1}{\sqrt{N}}$.

Transitions can be treated in the same way as for the U(2) model discussed in the preceding section [20].

IV. U(4) × U(4) VIBRON MODEL: LINEAR MOLECULES

A. Energy spectra

A triatomic molecule is described in the vibron model by the combined groups U(4) × U(4). The picture is that each U(4) group describes the properties of a single bond, and that terms involving operators drawn from both U(4) groups describe the coupling between the bonds. In this paper we consider parameter choices for this description appropriate to linear triatomic molecules in the $\mathrm{U}(4)\times\mathrm{U}(4)\supset\mathrm{O}(4)\times\mathrm{O}(4)\supset\mathrm{O}_{12}(4)\supset\mathrm{O}_{12}(3)$ group chain. We will return to bent molecules in a later paper [23]. The U(4) groups are realized with two sets of commuting bosons, $s_1, \mathbf{p}_1$ and $s_2, \mathbf{p}_2$. The Hamiltonian for the triatomic molecule is taken to be

$$\begin{aligned} H = & -A_1C_2(\mathrm{O}_1(4)) + B_1C_2(\mathrm{O}_1(3)) - A_2C_2(\mathrm{O}_2(4)) \\ & +B_2C_2(\mathrm{O}_1(3)) - A_{12}C_2(\mathrm{O}_{12}(4)) \\ & +\lambda\mathcal{M}_{12} + BC_2(\mathrm{O}_{12}(3)), \end{aligned} \tag{26}$$

where the Casimir invariants of the combined O(4) and O(3) groups are given in terms of the combined dipole operator $\mathbf{D}_{12} = \mathbf{D}_1 + \mathbf{D}_2$ and total angular momentum operator $\mathbf{L}_{12} = \mathbf{L}_1 + \mathbf{L}_2$. In terms of the bosons, the Majorana operator $\mathcal{M}_{12}$ is given by

$$\mathcal{M}_{12} = (\mathbf{p}_1^\dagger s_2^\dagger - s_1^\dagger \mathbf{p}_2^\dagger)\cdot(\mathbf{p}_1 s_2 - s_1\mathbf{p}_2) + (\mathbf{p}_1^\dagger \times \mathbf{p}_2^\dagger)\cdot(\mathbf{p}_1 \times \mathbf{p}_2). \tag{27}$$

Note that the Hamiltonian commutes separately with the number operator for each boson type, $\hat{N}_i = s_i^\dagger s_i + \mathbf{p}_i^\dagger \cdot \mathbf{p}_i$. For future reference we prefer to rewrite the O(3) parts of the Hamiltonian as

$$\begin{aligned} H = & -A_1C_2(\mathrm{O}_1(4)) - A_2C_2(\mathrm{O}_2(4)) - A_{12}C_2(\mathrm{O}_{12}(4)) \\ & +\lambda\mathcal{M}_{12} + B_L L^2 + B_\Delta \Delta^2 + B_{L\Delta}\mathbf{L}\cdot\mathbf{\Delta}, \end{aligned} \tag{28}$$

where $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ and $\mathbf{\Delta} = \sqrt{\frac{N_2}{N_1}}\mathbf{L}_1 - \sqrt{\frac{N_1}{N_2}}\mathbf{L}_2$. The operator created by $\mathbf{\Delta}$ is not a spin, but rather is the kinetic part of the bending mode. It is analogous to a similar operator in the description of the scissors mode in nuclear physics [24].

We now wish to solve this Hamiltonian using the MFA. Because each boson number is separately conserved, we introduce a condensate boson for each boson type by

$$b_{ci} = \frac{1}{\sqrt{1+r_i^2}}(s_i + \mathbf{r}_i\cdot\mathbf{p}_i) \tag{29}$$

and use a product of mean-field states as a variational estimate,

$$|N_1,\mathbf{r}_1;N_2,\mathbf{r}_2\rangle = \frac{1}{\sqrt{N_1!N_2!}}[(b_{c1}^\dagger)^{N_1}][(b_{c2}^\dagger)^{N_2}]|0\rangle, \tag{30}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the variational parameters. We take the expectation value of the Hamiltonian in the condensate and find (noting that the angular momentum operators always have zero expectation value in the condensate)

$$\begin{aligned} \langle N_1,\mathbf{r}_1;N_2,\mathbf{r}_2|H|N_1,\mathbf{r}_1;N_2,\mathbf{r}_2\rangle = & -(A_1+A_{12})\frac{4N_1^2r_1^2}{(1+r_1^2)^2} - (A_2+A_{12})\frac{4N_2^2r_2^2}{(1+r_2^2)^2} - 8A_{12}\frac{N_1N_2\mathbf{r}_1\cdot\mathbf{r}_2}{(1+r_1^2)(1+r_2^2)} \\ & +\lambda\frac{N_1N_2}{(1+r_1^2)(1+r_2^2)}[(\mathbf{r}_1-\mathbf{r}_2)^2 + (\mathbf{r}_1\times\mathbf{r}_2)^2]. \end{aligned} \tag{31}$$

The expectation value of the Hamiltonian in the condensate depends on the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, which we call θ. Solving for the minimum energy with respect to that angle we find two roots, $\sin\theta = 0$ and $\cos\theta = -(4A_{12}+\lambda)/\lambda r_1 r_2$. For a linear molecule one typically uses [4] parameters where $|-(4A_{12}+\lambda)/\lambda r_1 r_2| > 1$, which shows that we should only have a solution $\theta = 0$ or $\theta = \pi$, which corresponds to a linear molecule. One can also show that for the parameters considered here, the mean-field minimum comes at $r_1 = r_2 = 1$ and $\theta = 0$. To make the r's different requires some combination of a large λ (strong Majorana term) and additional terms proportional to $C_2(\mathrm{U}(3))$ in one or both of the bosons. We do not introduce such terms here, since we restrict ourselves to the $\mathrm{O}(4)\times\mathrm{O}(4)$ limit where $r_i = 1$.

To study quantum fluctuations around the condensate, we introduce the orthogonal fluctuation bosons. As before we take the molecular symmetry axis along z. For the $r = 1$ case, the FB's are just as in the single U(4) case. Explicitly, $b_{zi} = \frac{1}{\sqrt{2}}(-s_i + p_{zi})$, $b_{xi} = p_{xi}$, and $b_{yi} = p_{yi}$. We rewrite the Hamiltonian (up to constant terms) in terms of the condensate bosons and the FB's and make the substitutions of (22) and (23) for each boson type to find

$$\begin{aligned} H = {} & [4(A_1 + A_{12})N_1 + (4A_{12} + \lambda)N_2]\, b^\dagger_{z1} b_{z1} + [4(A_2 + A_{12})N_2 + (4A_{12} + \lambda)N_1]\, b^\dagger_{z2} b_{z2} \\ & -\lambda\sqrt{N_1 N_2}(b^\dagger_{z1} b_{z2} + b^\dagger_{z2} b_{z1}) + (2A_{12} + \lambda)(N_1 + N_2)\left[b^\dagger_{xB} b_{xB} + b^\dagger_{yB} b_{yB}\right] + B_\Delta \left[\Delta_x^2 + \Delta_y^2\right] \\ & + B_L \left[L_x^2 + L_y^2\right] + B_{L\Delta}\left[L_x \Delta_x + L_y \Delta_y\right], \end{aligned} \qquad (32)$$

where we have introduced the bosons that create and destroy the bending modes. In terms of the b_{xi} they are given by

$$b^\dagger_{xB} = \frac{\sqrt{N_2} b^\dagger_{x1} - \sqrt{N_1} b^\dagger_{x2}}{\sqrt{N_1 + N_2}} \qquad (33)$$

with a similar expression for the y bending mode. These are closely related to Δ:

$$\Delta_x = \frac{i}{\sqrt{2}}\left(b^\dagger_{xB} - b_{xB}\right). \qquad (34)$$

Finally we also introduce the intrinsic components of the angular momentum

$$L_x = \frac{i}{\sqrt{2}}\left[\sqrt{N_1}(b^\dagger_{x1} - b_{x1}) + \sqrt{N_2}(b^\dagger_{x2} - b_{x2})\right], \qquad (35)$$

and similarly for L_y. Even though the rotational and the vibrational modes are not decoupled in the Hamiltonian (32), we can do so by making a canonical transformation [23]. Clearly there are two degenerate bending modes, one in the yz plane generated by $b^\dagger_{xB}$ and another in the xz plane generated by $b^\dagger_{yB}$. The explicit form of the bending modes is completely determined from the geometry. The bending modes have frequency $(2A_{12} + \lambda)(N_1 + N_2)$, so that they are generated from a mixture of the mixed O(4) term (A_{12}) and the Majorana term. In the same part of the Hamiltonian we also find the rotational zero modes, corresponding to a rotation around the x or y axis. There is a dynamical coupling between the bending and rotational modes, $B_{L\Delta}$. This term is well known in the mean-field limit of the nuclear analog of the vibron model [24]. We also see that there are two stretching modes carried by the b_z bosons. Only the Majorana term mixes the stretching modes of the two types. The resulting 2×2 matrix can be diagonalized. Thus in total we have six harmonic modes of a linear triatomic molecule.

The same result could be obtained using RPA matrices discussed in Appendix A. Here one introduces complex classical variables for each U(4) bosons. Since this procedure is straightforward, we do not go into more detail.

In order to show the power of the discussion given above let us compare our results for linear triatomic molecules with those obtained in [4]. The Hamiltonian used in that paper contains terms quadratic in the Casimir operators, beyond the terms used in (28). Fortunately these terms are constructed in such a way that the higher-order terms vanish in the harmonic limit. In Table II we compare the harmonic energies with the exact vibrational levels using the parameters in Table I from Fit III in [4].

TABLE II. A comparison of the exact vibron model calculation to the harmonic approximation: linear triatomic molecules.

$v_1 v_2^{l_2} v_3$	Exact	MFA	Error
	HCN ($N_1 = 140, N_2 = 47$)		
01^10	712.4	707.8	0.65%
10^00	2095.8	2092.1	0.18%
00^01	3312.6	3318.0	0.16%
	OCS ($N_1 = 190, N_2 = 159$)		
01^10	519.4	518.3	0.21%
10^00	860.2	861.8	0.19%
00^01	2062.2	2064.9	0.13%
	N_2O ($N_1 = 163, N_2 = 134$)		
01^10	588.9	586.9	0.34%
10^00	1284.9	1270.7	1.1%
00^01	2223.6	2224.9	0.06%
	$C^{12}O_2$ ($N_1 = N_2 = 153$)		
01^10	666.8	664.0	0.42%
10^00	1388.4	1339.1	3.5%
00^01	2348.3	2350.7	0.10%
	$C^{13}O_2$ ($N_1 = N_2 = 154$)		
01^10	648.6	645.0	0.56%
10^00	1370.1	1333.6	2.6%
00^01	2283.2	2284.7	0.07%

TABLE III. A comparison of the exact vibron model calculation to the harmonic approximation plus Fermi coupling.

$v_1 v_2^{l_2} v_3$	Exact	MFA	Error
	$C^{12}O_2$ ($N_1 = N_2 = 153$)		
01^10	666.8	664.0	0.42%
10^00	1388.4	1384.0	0.32%
00^01	2348.3	2350.7	0.10%
	$C^{13}O_2$ ($N_1 = N_2 = 154$)		
01^10	648.6	645.0	0.56%
10^00	1370.1	1362.7	0.53%
00^01	2283.2	2284.7	0.07%

Our boson expansion results agree very well with the exact calculation. The only large errors appear in the $(v_1 v_2^{l_2} v_3) = (10^0 0)$ states of the two isotopic CO_2 molecules. These are due to the well-known Fermi resonances which arise from the coupling between the nearly degenerate $(02^0 0)$ and $(10^0 0)$ states. When the operator effecting this coupling is included [as defined in Eq. (2.14) of [4], it has strength $(x_{12} - 1)\lambda$], the stretching modes are given by the following matrix for the states $(02^0 0), (10^0 0), (00^0 0)$:

$$\begin{pmatrix} (4A_{12} + 2\lambda)(N_1 + N_2) & -x_{12}\lambda \frac{N_1+N_2}{\sqrt{N_1}} & -x_{12}\lambda \frac{N_1+N_2}{\sqrt{N_2}} \\ -x_{12}\lambda \frac{N_1+N_2}{\sqrt{N_1}} & 4(A_1 + A_{12})N_1 + 4A_{12}N_2 + \lambda N_2 & -\lambda\sqrt{N_1 N_2} \\ -x_{12}\lambda \frac{N_1+N_2}{\sqrt{N_2}} & -\lambda\sqrt{N_1 N_2} & 4(A_2 + A_{12})N_2 + 4A_{12}N_1 + N_1 \end{pmatrix} . \qquad (36)$$

The improved results for CO_2 molecules are shown in Table III. From these two tables we see that the MFA (equivalently the RPA) gives excellent results for the transition energies, particularly if the Fermi term is included. The agreement between the exact and MFA results is at least as good as one would expect for a $1/N$ expansion.

B. Transitions

While we can obtain the energy spectra accurately and easily by using the MFA, the application of the same technique to transitions is less satisfactory. There are two reasons for this. First, calculation of transition intensities requires accurate knowledge of the wave functions of the molecules. In the MFA, the error for the wave function is $1/\sqrt{N}$. For a typical polyatomic molecule, this is about 10%. Therefore we make a much larger error for transition intensities than for energy spectra by using the MFA. Second, the transition intensities associated with different modes of a molecule may have very disparate strengths. This signals strong cancellations and a rather special transition operator. Take HCN, for example, the intensity (in units of cm/molecule) for the transition from (100) to the ground state is about 0.5 while that for (001) is 988. Moreover the intensity for (002) is 9.9, which is about two orders of magnitude less than (001). The error arising from the use of the MFA far exceeds the accuracy required for calculations of these weak transitions. Nevertheless, as the transition intensities provide important and more stringent conditions on a model Hamiltonian, we would like to study the transition intensities in the MFA of the vibron model so as to gain some qualitative insights for the model from transition measurements. In view of the difficulties we mentioned above, we limit ourselves to transitions involving at most two quanta since higher transitions are strongly affected by anharmonicities of the wave functions.

As an example, we shall study the vibrational transitions associated with the stretching modes of HCN. These transitions have been exposed to detailed theoretical and experimental scrutiny [25]. Of special interest is the surprisingly slow decrease of transition strength with the vibrational quantum number.

For each vibron u(4) algebra, we take the vibrational dipole operator to be

$$\mathbf{T}_i = \gamma_i^0 \mathbf{D} + \gamma_i^1 (\mathbf{D} e^{-\alpha_i \hat{N}_{pi}} + e^{-\alpha_i \hat{N}_{pi}} \mathbf{D}) \quad (i = 1, 2), \qquad (37)$$

where the first term contributes only to the static dipole moment in the O(4) limit and the second term induces vibrational dipole transitions. The total dipole operator is assumed to be the sum

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2. \qquad (38)$$

This form, although often used [26], is almost certainly too simple since we neglect the cross polarizability of the bonds [25]. Let the creation operators for the two stretching modes be $a_1^\dagger$ and $a_2^\dagger$; we have

$$\begin{aligned} b_{z1}^\dagger &= (\cos\phi) a_1^\dagger + (\sin\phi) a_2^\dagger, \\ b_{z2}^\dagger &= -(\sin\phi) a_1^\dagger + (\cos\phi) a_2^\dagger, \end{aligned} \qquad (39)$$

where ϕ is the mixing angle between normal and local modes. The transition intensities are given by

$$I_{(0)\to(v)} = \frac{8\pi^3}{3hc} \omega |\langle v|\mathbf{T}|0\rangle|^2, \qquad (40)$$

where (0) is the ground state and $(v) = (v_1 v_2 v_3)$ is the excited vibrational state.

Since we shall only consider excited stretching states with $v_2 = 0$, we can simplify (38) in the MFA to get (since we are considering the case $r = 1$ the operator $\mathbf{D}$ does not contribute to the transitions)

$$\begin{aligned} T_{v_1,v_3} = \frac{1}{\sqrt{v_1! v_3!}} [\, & F_1 \rho_1^{v_1+v_3} \cos^{v_1}\phi \sin^{v_3}\phi \\ & + F_2 \rho_2^{v_1+v_3} (-\sin\phi)^{v_1} \cos^{v_3}\phi], \end{aligned} \qquad (41)$$

where $T_{v_1,v_3} = \langle (v)|T_z|(0)\rangle$ is the matrix element of the dipole operator and

$$\begin{aligned} F_1 &= 2N_1 \gamma_1^1 e^{-\frac{\alpha_1}{2}N_1 + \frac{\alpha_1^2}{8}N_1}, \\ F_2 &= 2N_2 \gamma_2^1 e^{-\frac{\alpha_2}{2}N_2 + \frac{\alpha_2^2}{8}N_2}, \\ \rho_1 &= -\frac{\alpha_1}{2}\sqrt{N_1}, \quad \rho_2 = -\frac{\alpha_2}{2}\sqrt{N_2}. \end{aligned}$$

We can determine the four parameters in the dipole operator as well as the mixing angle ϕ by using the transition intensities of (100), (001), (200), (101), and (002). Of course one can also determine ϕ from the Hamiltonian;

we would like to consider the value obtained from the transition operators as a constraint on the Hamiltonian, as discussed below.

Due to the sign ambiguity for the matrix elements, we can have many sets of solutions. Since the mixing angle is a more important quantity for the wave function, we will concentrate on ϕ. After some algebra, we can show that one of solutions is given by

$$\tan\phi = B + \sqrt{B^2+1} \tag{42}$$

with $B = (T_{02} - T_{20})/(\sqrt{2}T_{11})$. Choosing signs for the matrix elements such that $B = -1.229$, we find $\phi_0 = 20°$. Other possible solutions for ϕ are $\phi = \pm\phi_0 + n\pi/2$, where n is an integer. Using this solution with $\phi_0 = 20°$, we calculate the transition intensities for higher vibrational levels and the results are given in Table IV, which do not reproduce the slow decrease of intensities in the data.

When we diagonalize the mean-field Hamiltonian (32) using the parameters in Table I from Fit III in [4], we find $\phi = 0.59°$, which is very different from ϕ_0. Since the transition data are less accurate and we have used a very simple dipole operator, this discrepancy needs further examination.

For this purpose, we use an old-fashioned mechanical model for polyatomic molecules [26] to study the wave function of the HCN stretching modes. Let us label the atoms in HCN in the order of 2-3-1. Then we define the c.m. coordinate and bond-stretching coordinates as

$$R = \frac{m_1z_1 + m_2z_2 + m_3z_3}{m_1+m_2+m_3}, \tag{43}$$

$$r_1 = z_1 - z_3 - L_{\text{CN}}, \tag{44}$$

$$r_2 = z_3 - z_2 - L_{\text{CH}}, \tag{45}$$

where L_{CH} and L_{CN} are the equilibrium bond lengths. In terms of these new coordinates, the kinetic energy of the molecule becomes

$$T = \tfrac{1}{2}M\dot{R}^2 + \tfrac{1}{2}\mu_1\dot{r}_1^2 + \tfrac{1}{2}\mu_2\dot{r}_2^2 + \mu_{12}\dot{r}_1\dot{r}_2, \tag{46}$$

where $M = m_1+m_2+m_3$ is the mass of the molecule and $\mu_1 = m_1(m_2+m_3)/M$, $\mu_2 = m_2(m_1+m_3)/M$, and $\mu_{12} = m_1m_2/M$ are the reduced masses. The first term in (46) is the c.m. kinetic energy and will not be considered from now on. Adding a harmonic potential energy, we have the Hamiltonian

$$H = \tfrac{1}{2}\mu_1\dot{r}_1^2 + \tfrac{1}{2}\mu_2\dot{r}_2^2 + \mu_{12}\dot{r}_1\dot{r}_2 + \tfrac{1}{2}k_1r_1^2 + \tfrac{1}{2}k_2r_2^2 + k_{12}r_1r_2. \tag{47}$$

We now make a change of dynamical variables from r_1, r_2 to ρ_1, ρ_2 through the transformation

$$\begin{aligned} r_1 &= \eta(\rho_1\cos\varphi + \rho_2\sin\varphi), \\ r_2 &= -\rho_1\sin\varphi + \rho_2\cos\varphi, \end{aligned} \tag{48}$$

where the parameters η, φ are chosen to be

$$\eta = -\sqrt{\frac{k_2\mu_{12} - \mu_2k_{12}}{k_1\mu_{12} - \mu_1k_{12}}} \tag{49}$$

and

$$\tan 2\varphi = \frac{2\mu_{12}\eta}{\mu_2 - \mu_1\eta^2}. \tag{50}$$

The Hamiltonian H is thus reduced to a sum of the Hamiltonians of two decoupled harmonic oscillators

$$H = \tfrac{1}{2}M_1\dot{\rho}_1^2 + \tfrac{1}{2}K_1\rho_1^2 + \tfrac{1}{2}M_2\dot{\rho}_2^2 + \tfrac{1}{2}K_2\rho_2^2, \tag{51}$$

where the diagonal masses and force constants are

$$\begin{aligned} M_1 &= \mu_1\eta^2\cos^2\varphi + \mu_2\sin^2\varphi - \mu_{12}\eta\sin 2\varphi, \\ M_2 &= \mu_1\eta^2\sin^2\varphi + \mu_2\cos^2\varphi + \mu_{12}\eta\sin 2\varphi, \\ K_1 &= k_1\eta^2\cos^2\varphi + k_2\sin^2\varphi - k_{12}\eta\sin 2\varphi, \\ K_2 &= k_1\eta^2\sin^2\varphi + k_2\cos^2\varphi + k_{12}\eta\sin 2\varphi. \end{aligned} \tag{52}$$

Using the values given in [26] for the force constants (in 10^5dyn/cm)

$$k_1 = 18.6, \quad k_2 = 5.7, \quad k_{12} = -0.22, \tag{53}$$

we find the normal mode frequencies to be $\omega_1 = \sqrt{K_1/M_1} = 2109.6$ cm^{-1} and $\omega_2 = \sqrt{K_2/M_2} = 3296.9$ cm^{-1}, in close agreement with experiment. We also find $\varphi = 15°$ and $\eta = -0.534$.

Now let us introduce creation and annihilation operators for these modes $(c_1, c_1^\dagger)$ and $(c_2, c_2^\dagger)$. The coordinates are related to them by

$$\rho_1 = \sqrt{\frac{\hbar}{2M_1\omega_1}}(c_1 + c_1^\dagger), \quad \rho_2 = \sqrt{\frac{\hbar}{2M_2\omega_2}}(c_2 + c_2^\dagger). \tag{54}$$

We can make a connection between the mechanical model and the vibron model by identifying the creation operators for the normal modes in these two models:

$$c_1 = a_1, \quad c_2 = a_2. \tag{55}$$

This then allows us to relate r_1, r_2 to the vibron bosons as follows:

TABLE IV. Transition intensities of HCN (in units of cm/molecule). Numbers in brackets denote powers of 10.

Level	Energy (cm^{-1})	Expt.	Calc.
10^00	2096.9	0.5	0.5 (input)
00^01	3311.5	988	988 (input)
20^00	4173.1	2.7[-3]	2.7[-3] (input)
10^01	5393.7	2.6	2.6 (input)
00^02	6519.6	9.9	9.9 (input)
30^00	6220.7	2.2[-3]	1.1[-5]
20^01	7441.6	1.6[-3]	2.9[-3]
10^02	8585.6	6.6[-2]	2.4[-2]
00^03	9627.0	0.16	0.067
30^01	9479.2	5.5[-4]	2.1[-6]
20^02	10618.9	3.4[-4]	2.4[-5]
10^03	11674.5	4.3[-3]	1.4[-4]
00^04	12635.9	6.6[-3]	3.0[-4]

$$r_1 = \eta\left(\sqrt{\frac{\hbar}{2M_1\omega_1}}\cos\varphi\cos\phi + \sqrt{\frac{\hbar}{2M_2\omega_2}}\sin\varphi\sin\phi\right)(b_{z1} + b_{z1}^\dagger)$$
$$+\eta\left(-\sqrt{\frac{\hbar}{2M_1\omega_1}}\cos\varphi\sin\phi + \sqrt{\frac{\hbar}{2M_2\omega_2}}\sin\varphi\cos\phi\right)(b_{z2} + b_{z2}^\dagger), \tag{56}$$

$$r_2 = \left(-\sqrt{\frac{\hbar}{2M_1\omega_1}}\sin\varphi\cos\phi + \sqrt{\frac{\hbar}{2M_2\omega_2}}\cos\varphi\sin\phi\right)(b_{z1} + b_{z1}^\dagger)$$
$$+\left(\sqrt{\frac{\hbar}{2M_1\omega_1}}\sin\varphi\sin\phi + \sqrt{\frac{\hbar}{2M_2\omega_2}}\cos\varphi\cos\phi\right)(b_{z2} + b_{z2}^\dagger). \tag{57}$$

It is easy to see that if the following condition is satisfied,

$$\sqrt{M_1\omega_1} = \sqrt{M_2\omega_2}, \tag{58}$$

we can eliminate the $(b_{z2} + \text{H.c.})$ term from (56) and the $(b_{z1} + \text{H.c.})$ term from (57) *simultaneously* by setting $\tan\phi = \tan\varphi$. The vibron model has a clear geometrical relation to the mechanical model. Since $M_1\omega_1 = \sqrt{M_1K_1}$ and $M_2\omega_2 = \sqrt{M_2K_2}$, we could define the following ratio R as a measure of the difference between vibron model and the mechanical model,

$$R = \left(\frac{M_1K_1}{M_2K_2}\right)^{1/4}. \tag{59}$$

For HCN, we have found that $R = 1.197$, which is close to 1. This means that ϕ should be close to 15°. This agrees qualitatively with what we obtained from transitions. From the mean-field Hamiltonian (33), we could get such a relative large mixing by using the following set of parameters ($N_1 = 140, N_2 = 47$):

$$A_1 = -0.844,\quad A_2 = 4.947,\quad A_{12} = 3.779,\quad \lambda = -3.75. \tag{60}$$

This set also produces correctly the harmonic spectra of HCN and may be preferable to the parameters used in [4].

In general, R could be very different from 1 and then it is not possible to relate the mean-field Hamiltonian in the O(4) limit to that of the mechanical model. In order to make such a connection, it is necessary that the mean-field Hamiltonian of the vibron model have terms of the type $b_{z1}^\dagger b_{z2}^\dagger + b_{z1}b_{z2}$. We could obtain such a Hamiltonian by adding $C_2(\text{U}(3))$ interactions.

V. U(4)×U(4)×U(4) VIBRON MODEL: LINEAR FOUR-ATOM MOLECULES

For four-atom molecules the appropriate group structure is U(4)×U(4)×U(4). Again the picture is that each U(4) group describes the properties of a single bond, and that bond coupling is realized in terms of operators drawn from different U(4) groups. The U(4) groups are realized in terms of three sets of commuting bosons, $s_i, \mathbf{p}_i$. In this work we will only consider parameters appropriate to linear four-atom molecules of the structure $ABBA$, e.g., acetylene (HCCH). In terms of the boson labels we take $i = 1, 2$ for the two A–B bonds and $i = 3$ for the B–B bond. Our Hamiltonian will commute with the number operator for each boson type, and the symmetry of the molecule requires $N_1 = N_2$. We take for our Hamiltonian

$$\begin{aligned} H = &-A_1C_2(\text{O}_1(4)) - A_2C_2(\text{O}_2(4)) \\ &-A_3C_2(\text{O}_3(4)) - A_{12}C_2(\text{O}_{12}(4)) \\ &-A_{123}C_2(\text{O}_{123}(4)) + \lambda\mathcal{M}_{12} + BC_2(\text{O}_{123}(3)), \end{aligned} \tag{61}$$

where the symmetry of the molecule will require that $A_1 = A_2$ and where $C_2(\text{O}_{123}(3)) = L^2$ with $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2 + \mathbf{L}_3$. We take parameters such that the molecule is linear and the condensate has $r_1 = r_2 = r_3 = 1$. As usual we take the axis of the molecule in the z direction. We introduce the orthogonal fluctuation bosons and find

$$C_2(\text{O}_i(4)) \rightarrow N_i^2 - 4N_ib_{zi}^\dagger b_{zi}, \tag{62}$$

$$\begin{aligned} C_2(\text{O}_{12}(4)) \rightarrow\, & C_2(\text{O}_1(4)) + C_2(\text{O}_2(4)) \\ &-(4N_1 + 2N_2)b_{z1}^\dagger b_{z1} - (4N_2 + 2N_1)b_{z2}^\dagger b_{z2} \\ &-\sqrt{N_1 + N_2}(b_{xB}^\dagger b_{xB} + b_{yB}^\dagger B_{yB}) \end{aligned} \tag{63}$$

[in terms of the bending bosons of (33)],

$$\begin{aligned} \mathcal{M}_{12} \rightarrow\, & N_2b_{z1}^\dagger b_{z1} - N_1b_{z2}^\dagger b_{z2} - \sqrt{N_1N_2}(b_{z1}^\dagger b_{z2} + b_{z2}^\dagger b_{z1}) \\ &+(N_1 + N_2)(b_{xB}^\dagger b_{xB} + b_{yB}^\dagger B_{yB}), \end{aligned} \tag{64}$$

TABLE V. A comparison of the exact vibron model calculation to the harmonic approximation: linear four-atom molecules.

$v_1v_2v_3; v_4^{l_4}v_5^{l_5}$	Exact	MFA	Error
	HCCH ($N_1 = N_2 = 43, N_3 = 137$)		
$100; 0^00^0$	3286.93	3286.73	0.00%
$001; 0^00^0$	3366.88	3368.42	0.05%
$010; 0^00^0$	1975.80	1983.68	0.40%
$000; 1^10^0$	617.12	611.20	0.96%
$000; 0^01^1$	724.50	717.21	1.00%
	DCCD ($N_1 = N_2 = 61, N_3 = 137$)		
$100; 0^00^0$	2435.58	2430.44	0.21%
$001; 0^00^0$	2706.35	2704.44	0.07%
$010; 0^00^0$	1769.57	1769.18	0.02%
$000; 1^10^0$	513.55	510.80	0.05%
$000; 0^01^1$	534.08	528.79	0.99%

and finally for $C_2(\mathrm{O}_{123}(4))$ in what is an obvious notation

$$C_{123} = C_{12} + C_{23} + C_{13} - C_1 - C_2 - C_3, \tag{65}$$

where C_{23} (C_{13}) can be obtained from C_{12} by making the proper replacements. For the rotational energy we have

$$C_2(\mathrm{O}_{123}(3)) \rightarrow L_x^2 + L_y^2, \tag{66}$$

with

$$L_x = \frac{i}{\sqrt{2}}\left[\sqrt{N_1}(b_{x1}^\dagger - b_{x1}) + \sqrt{N_2}(b_{x2}^\dagger - b_{x2}) + \sqrt{N_3}(b_{x3}^\dagger - b_{x3})\right] \tag{67}$$

and similarly for L_y.

From the MFA, we find three stretching modes, two doubly degenerate bending modes, and two zero modes. In Table V, we compare our results with the exact ones given in [5] (the parameters are taken from Table II in [5]). Again we find excellent agreement.

VI. DISCUSSION AND SUMMARY

Mean-field methods have been employed to study algebraic models by a number of groups [10–20]. In this work we apply the mean-field approximation (MFA) to the vibron model, an algebraic model for molecular dynamics. We show that the MFA gives a very accurate description of the molecular spectra and provides a closer geometrical picture of the molecular modes. The success of the MFA is ensured by the large-N values in vibron models (on the order of 100).

Our boson expansion method is similar to that used in [17] in a nuclear physics context. However, our prescription (22) and (23) allows us to avoid calculating commutators. This not only reduces the computational effort, but also provides us with a direct way of obtaining the MFA Hamiltonian quadratic in the fluctuation bosons. The use of the RPA ensures an automatic separation between intrinsic and zero modes.

The MFA also provides a convenient vehicle in which to seek the link between the algebraic operators and the geometrical molecular coordinates. By studying this connection, we can obtain valuable insights into the vibron models. In Sec. IV B, we showed that under a certain condition [see (59)], we can indeed identify the vibron model bosons with the underlying geometrical coordinates. These conditions can serve as a guide to select interactions terms for the full vibron Hamiltonian. In the future we will also investigate the role of $C_2(\mathrm{U}(3))$ that can shift the minimum from the O(4) limit $r = 1$. Information of molecular structures is contained not only in the spectra of molecules but also in their wave functions. The most detailed knowledge on wave functions comes mainly from transition intensities. We have attempted to study the transitions of HCN in the MFA. Although the result is plagued by the large error in the transition calculation, we have found that the mixing of two local vibron stretching modes is large. While a better understanding of transition intensities is clearly called for, in the future we will study the anharmonic corrections to the MFA calculation of transition intensities.

We here proposed in this work a relation [see (25)] involving the bond length and the anharmonic constant of a molecule that seems to work well for many diatomic molecules. A plausible argument leading to this relation is provided with the aid of the MFA.

We have concentrated in this work on linear molecules. We will apply the techniques developed here to bent triatomic molecules and more complex molecules in a future presentation [23]. There we also intend to study the bond length and moments of inertia using the MFA of vibron model in greater detail.

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APPENDIX A: RPA MATRICES

In the boson expansion method we have used so far, we first determine the optimal condensate boson by minimizing the expectation value of the Hamiltonian in the condensate and construct its orthogonal fluctuation bosons. With the prescription (22) and (23), we then obtain the MFA Hamiltonian which is quadratic in the fluctuation bosons. Its spectra is harmonic and, as we have shown, reproduces accurately the energy levels of the full Hamiltonian when the boson numbers N are large. In this appendix, we briefly outline an equivalent formulation in terms of *complex* classical variables and demonstrate how it is related to the boson expansion method.

We use the case of the U(4) model given by (14) in Sec. III as an example. We start again with determining the optimal condensate boson and a set of orthogonal fluctuation bosons. We then take a general trial wave function

$$|[N]\beta,\beta^*\rangle = \frac{1}{\sqrt{N!}}\Gamma_0^{\dagger N}|0\rangle, \tag{A1}$$

with

$$\Gamma_0^\dagger = \sqrt{1-|\beta|^2}b_c^\dagger + \beta\cdot b^\dagger. \tag{A2}$$

By construction, the expectation value of the Hamiltonian

$$E(\beta,\beta^*) = \langle[N]\beta,\beta^*|\frac{H}{N}|\beta,\beta^*\rangle \tag{A3}$$

has a minimum at $\beta = \beta^* = 0$ and an expansion in β and β^* around it is thus very easy.

We obtain $E(\beta,\beta^*)$ by substituting in (14) the following relations:

$$\begin{aligned} s &\rightarrow \sqrt{\tfrac{N}{2}}(\sqrt{1-|\beta|^2} - \beta_z),\\ p_z &\rightarrow \sqrt{\tfrac{N}{2}}(\sqrt{1-|\beta|^2} + \beta_z),\\ p_x &\rightarrow \sqrt{N}\beta_x,\\ p_y &\rightarrow \sqrt{N}\beta_y \end{aligned} \tag{A4}$$

(for creation operators, we take the complex conjugate of the right side). Keeping only quadratic terms in $\boldsymbol{\beta}$ and $\boldsymbol{\beta}^*$, we find

$$E(\beta,\beta^*) = 4AN\beta_z^*\beta_z - \frac{BN}{2}[(\beta_x^*-\beta_x)^2+(\beta_y^*-\beta_y)^2]. \tag{A5}$$

This is equivalent to (24). In fact, we could obtain (A5) by rewriting (14) in terms of the condensate and fluctuation bosons and then making the appropriate substitutions. For fluctuation bosons, we simply use

$$\mathbf{b} \to \boldsymbol{\beta}, \mathbf{b}^\dagger \to \boldsymbol{\beta}^*. \tag{A6}$$

For condensate bosons, we use

$$b_c(b_c^\dagger) \to \sqrt{N(1-|\boldsymbol{\beta}|^2)}. \tag{A7}$$

This last equation is equivalent to the prescription (22) and (23) in the MFA.

To calculate the harmonic spectrum of the classical Hamiltonian (70), we define the RPA matrices as

$$\mathcal{A} = \left.\frac{\partial^2 E}{\partial\beta^*\partial\beta}\right|_{\beta=\beta^*=0}, \tag{A8}$$

$$\mathcal{B} = \left.\frac{\partial^2 E}{\partial\beta^*\partial\beta^*}\right|_{\beta=\beta^*=0}. \tag{A9}$$

Thus we obtain

$$\mathcal{A} = \begin{pmatrix} BN & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & BN \end{pmatrix}, \tag{A10}$$

$$\mathcal{B} = \begin{pmatrix} -BN & 0 & 0 \\ 0 & 4AN & 0 \\ 0 & 0 & -BN \end{pmatrix}. \tag{A11}$$

Diagonalizing the product matrix $(\mathcal{B}-\mathcal{A})(\mathcal{B}+\mathcal{A})$, we find two zero eigenvalues and one positive eigenvalue $(4AN)^2$. The two zero eigenvalues correspond to the two rotational zero modes. The positive eigenvalue is equal to the square of the stretching mode ω_s^2. Thus we find $\omega_s = 4AN$ in agreement with the MFA result.

The above discussion can be extended to U(4)×U(4) and U(4)×U(4)×U(4) vibron models straightforwardly.

APPENDIX B: THE BOND LENGTH

To define the classical bond length in a diatomic molecule, one cannot use the coherent state of (20) directly. The classical state grows out of the quantum coherent state in the large-N limit, but to discuss displacements in states of finite N the quantum states must have a distribution in N. As N grows this distribution is more and more strongly peaked, but it must never be precise if we wish to discuss quantities such as displacements. States with just this property of being both displaced and having a distribution in N are the field coherent states. For a simple oscillator with a single boson type $(a, a^\dagger)$, the field coherent state is given by

$$|\lambda\rangle = e^{-\lambda^2/2}e^{\lambda a^\dagger}|0\rangle. \tag{B1}$$

If one defines the displacement operator for the system in the normal way by

$$D = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a) = x_0(a^\dagger + a), \tag{B2}$$

it is easy to show that $\langle\lambda|D|\lambda\rangle = 2\lambda x_0$. Expanding $|\lambda\rangle$ in states of fixed boson number $|N\rangle$, it is seen that for large λ the most likely state in that expansion has $\sqrt{N} = \lambda$ and that there is very little dispersion. It is also well known that the fractional dispersion in the expected value of D is very small for large λ. We have

$$(\langle\lambda|D^2 - (\bar{D})^2|\lambda\rangle)^{1/2}/\bar{D} = \frac{1}{\sqrt{2N}} \tag{B3}$$

in terms of the most likely N. Thus in the large-N limit the expected value of the square of the displacement is equal to the square of the average displacement. We exploit this fact by exporting it to the coherent states of fixed boson number of (20).

We define the z displacement for the diatomic molecule as

$$D_z = x_0(p_z^\dagger + p_z), \tag{B4}$$

where the m in x_0 is the reduced mass for the relative motion and the ω vibrational frequency obtained in the MFA. We find

$$\langle N,r|D_z^2|N,r\rangle = x_0^2\frac{2Nr^2}{1+r^2} \tag{B5}$$

from which we take

$$\bar{D}_z = \sqrt{\langle D_z^2\rangle} = \sqrt{\frac{\hbar N}{m\omega}}\frac{r}{\sqrt{1+r^2}}, \tag{B6}$$

which is the form for the bond length we use in Sec. III.

Other empirical relationships between bond length and molecular parameters have been given before [27], but we do not know any derivation of the relation suggested here.

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