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

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We propose an algebraic model for bent triatomic molecules and discuss its geometrical interpretation. We solve the model analytically for the special case of bent symmetric triatomic molecules in the mean-field approximation and study water as an example.

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I. INTRODUCTION

In this paper we continue the study, as started in our previous paper [1] (which we shall refer to as I), of mean-field techniques in the algebraic description of molecules. Recently Iachello and co-workers have applied the vibron model [2, 3] (as the algebraic approach is called) to linear triatomic [4], bent triatomic [5], linear four-atomic [6], and even more complex molecules [7] by employing an expansion in Casimir invariants of the dynamical group chains of the model that closely parallels the Dunham expansion. Their work has demonstrated that the vibron model, with fewer parameters, can give fits to the vibrational spectra and transition intensities of polyatomic molecules comparable to or better than those obtained through conventional potential approaches and the Dunham expansion method. The vibron model has also been used successfully to study electron scattering from molecules [8, 9] and similar algebraic model has been shown to be a fertile starting point for studies of nuclear reaction problems [10]. Unfortunately, the model is formulated in terms of bosonic degrees of freedom, which are relatively easy to handle, but are not straightforwardly related to the molecular geometry. The use of the mean-field approximation (MFA) [11–13] together with the harmonic expansion around the mean-field random-phase approximation (RPA) can be used to gain geometric insight into the structure of the vibron model. In I, we expressed the vibrational excitations in terms of the fluctuation bosons derived from the MFA of the vibron model and thus showed the close relationship between the vibron model and the mechanical model for linear triatomic molecules and we also evaluated the bond length of a diatomic molecule in terms of its vibron model parameters. In this paper, we apply this approach to bent triatomic molecules. The major problem we want to address here is how to describe the bond geometry in the algebraic language. Since the Hamiltonian used by Iachello and co-workers for bent molecules is an expansion in Casimir invariants near the O(4) limit and only supports linear condensates (we discuss this problem, which was first mentioned by Leviatan and Kirson [13], in Appendix A, where we not only find the condensate solution but also derive the energy spectrum in the large-N limit), we propose a Hamiltonian that includes Casimir invariants of the U(3) type. This Hamiltonian, as we will show, can produce condensate states with the correct bond geometries of bent molecules. Moreover, this Hamiltonian leads naturally to three rotational zero modes without fine tuning the interaction parameters. We use the combination of the MFA plus RPA, discussed in I, to obtain detailed information about the structure of the Hamiltonian and calculate the three fundamental vibrational energies, the three moments of inertia, and the intensities of dipole transitions from the ground state to the fundamental vibrational states. While we do not seek a detailed fit to the entire spectrum of a bent molecule, we demonstrate how an essentially unique parametrization of our Hamiltonian and transition operator can be obtained to serve as a starting point to search for more accurate Hamiltonians.

This paper, employing essentially the same method in the MFA as I, is rather technical. We therefore advise readers not familiar with the MFA applied to the vibron model to first study Ref. [1]. It is far more pedagogic and we do not repeat that explanatory material here.

In Sec. II we first present a general framework for bent molecules in the MFA. We then describe in Sec. III the analytic solution of the MFA Hamiltonian for the special case of symmetric bent molecules (X_2Y). In Sec. IV we study the water molecule H_2O in some detail. Finally we discuss directions for further work. The Hamiltonian used by Iachello and co-workers [3, 5] is studied in MFA in Appendix A. Some complicated coefficients in the analytic solution of Sec. III are relegated to Appendix B.

II. VIBRON MODEL FOR BENT TRIATOMIC MOLECULE

The vibron model was originally designed to describe diatomic molecules. One uses an interacting boson model [2] that contains the bound-state spectrum of the Morse potential [which can be described by an O(4) dynamical symmetry] as a limiting case. The simplest interacting boson model with this property is generated by the group U(4), and is usually realized in terms of four bosons s, p_x, p_y, and p_z. The total number of bosons is taken to be a constant of the motion. In some sense only the **p** bosons are independent, and they are in one-to-one correspondence with the bond degrees of freedom of the molecule. This point is particularly clear in the MFA where the total boson number is large. We exploit that fact to connect the **p** "direction" with the bond angles in the bent molecule.

In the case of a polyatomic molecule, the vibron model [2, 3] can be constructed by associating a U(4) group with each independent bond of the molecule. In particular, for a triatomic molecule XYZ, which we want to study here, we choose a convenient set of two independent bonds, for example, XY and YZ, and assign a U(4) group to each bond. Let us designate these two groups as $\mathrm{U}_1(4)$ and $\mathrm{U}_2(4)$. Each $\mathrm{U}_i(4)$ ($i = 1$ or 2) group is realized in terms of four bosons s_i and $\mathbf{p}_i$. The vibron model Hamiltonian has the group structure $\mathrm{U}_1(4) \times \mathrm{U}_2(4)$ and conserves the boson number operator (N_i) of each U(4) group. [An alternative approach [13, 14] is to associate a U(4) group with each Jacobi coordinate, instead of with each bond. This approach has both advantages and disadvantages, but we will not pursue it here.]

Almost a decade ago, Iachello and co-workers [3] put forth a general algebraic formulation for triatomic molecules. The Hamiltonian was constructed as an expansion in powers of the following Casimir and Majorana operators

$$\begin{aligned}\hat{C}_1 &= C_2(\mathrm{O}_1(4)) - N_1(N_1+2),\\ \hat{C}_2 &= C_2(\mathrm{O}_2(4)) - N_2(N_2+2),\\ \hat{C}_{12} &= C_2(\mathrm{O}_{12}(4)) + a|C_2'(\mathrm{O}_{12}(4))| \\ &\quad -(N_1+N_2)(N_1+N_2+2),\\ \hat{M}_{12} &= (s_1^\dagger p_2^\dagger - s_2^\dagger p_1^\dagger)(s_1 p_2 - s_2 p_1) + (p_1^\dagger \times p_2^\dagger)(p_1 \times p_2),\end{aligned} \tag{1}$$

where $\mathrm{O}_i(4)(i = 1$ or 2) is the O(4) subgroup of $\mathrm{U}_i(4)$ generated by the angular momentum operators $\mathbf{L}_i = -i\mathbf{p}_i^\dagger \times \mathbf{p}_i$ and the dipole operators $\mathbf{D}_i = (s^\dagger \mathbf{p}_i + \mathbf{p}_i^\dagger s_i)$, the diagonal group $\mathrm{O}_{12}(4)$ is generated by $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ and $\mathbf{D} = \mathbf{D}_1 + \mathbf{D}_2$. The Casimir operator of O(4) is expressed in terms of its generators as $C_2(\mathrm{O}(4)) = \mathbf{L}\cdot\mathbf{L} + \mathbf{D}\cdot\mathbf{D}$. The operator $C_2'(\mathrm{O}_{12}(4)) = \mathbf{L}\cdot\mathbf{D}$ is the second Casimir invariant of the diagonal O(4) group. It is a pseudoscalar. Therefore it cannot appear linearly in a Hamiltonian. Its absolute value can, as used in Refs. [3, 5], but this is then no longer a two-body operator. For linear molecules the parameter a in $\hat{C}_{12}$ is taken to be 0. For bent molecules a has to be taken to be equal to 2. The Majorana operator $\hat{M}_{12}$ is a Casimir invariant of the diagonal $\mathrm{U}_{12}(4)$ group. Note that these operators preserve not only the total boson number, but also the number of bosons of each type.

The simplest Hamiltonian in terms of these operators is a linear combination of them

$$H = -A_1\hat{C}_1 - A_2\hat{C}_2 - A_{12}\hat{C}_{12} + \lambda\hat{M}_{12}. \tag{2}$$

For realistic application, higher-order terms are included [4, 5]. Such an expansion is similar to the familiar Dunham expansion and has been demonstrated to give equivalent or better fits to molecular vibrational spectra than the Dunham expansion [4, 5]. However, as we show in Appendix A, the underlying geometry of this type of Hamiltonians in the MFA corresponds to linear molecules, even for the Hamiltonian with $a = 2$ [3, 5], which is intended for a bent molecule.

In this work, we want to construct a geometrically correct vibron model Hamiltonian for bent triatomic molecules. Since the existence of a bent condensate requires three rotational zero modes, the Hamiltonian should be chosen such that it satisfies this condition. We go one step further and require that we produce a condensate state with the correct bond angle. A convenient way to do this is to include the Casimir and Majorana operators of U(3) subgroups: $\mathrm{U}_1(3), \mathrm{U}_2(3)$, and $\mathrm{U}_{12}(3)$. They are effectively represented by $\hat{n}_{p1}^2, \hat{n}_{p2}^2, \hat{n}_{p1}\hat{n}_{p2}$, and $(\mathbf{p}_1^\dagger \times \mathbf{p}_2^\dagger)\cdot(\mathbf{p}_1 \times \mathbf{p}_2)$. In contrast to [5] we wish to study the moments of inertia as well here and thus we also include rotational terms involving only the angular momentum operators: $\mathbf{L}_1^2, \mathbf{L}_2^2$, and $\mathbf{L}_1 \cdot \mathbf{L}_2$.

Since we are only interested in the MFA or the harmonic approximation of the vibron model, we limit the expansion in terms of the generators of the group $\mathrm{U}_1(4) \times \mathrm{U}_2(4)$ here to quadratic order. From the considerations outlined above, we take the Hamiltonian for a bent triatomic molecule to be

$$\begin{aligned}H =\ & A_1(\mathbf{L}_1\cdot\mathbf{L}_1 + \mathbf{D}_1\cdot\mathbf{D}_1) + A_2(\mathbf{L}_2\cdot\mathbf{L}_2 + \mathbf{D}_2\cdot\mathbf{D}_2) + A_{12}(\mathbf{L}_1\cdot\mathbf{L}_2 + \mathbf{D}_1\cdot\mathbf{D}_2)\\ &+\lambda(s_1^\dagger\mathbf{p}_2^\dagger - s_2^\dagger\mathbf{p}_1^\dagger)\cdot(s_1\mathbf{p}_2 - s_2\mathbf{p}_1) + \mu(\mathbf{p}_1^\dagger \times \mathbf{p}_2^\dagger)\cdot(\mathbf{p}_1 \times \mathbf{p}_2)\\ &+h_1 n_{p1}^2 + h_2 n_{p2}^2 + h_{12} n_{p1} n_{p2} + B_1 L_1^2 + B_2 L_2^2 + B_{12}\mathbf{L}_1\cdot\mathbf{L}_2.\end{aligned} \tag{3}$$

As discussed in I, in order to study the MFA of this Hamiltonian, we first construct its ground-state condensate. Since the boson number of each U(4) group is conserved, the condensate state takes the product form

$$|N_1, \mathbf{r}_1; N_2, \mathbf{r}_2\rangle = \frac{1}{\sqrt{N_1!N_2!}}(b_{c1}^\dagger)^{N_1}(b_{c2}^\dagger)^{N_2}\,|0\rangle\,, \tag{4}$$

where N_i is the boson number for the $\mathrm{U}_i(4)$ group ($i = 1$ or 2) and b_{c1} and b_{c2} are the condensate bosons for the two U(4) groups. The condensate boson of each type is given by

$$b_{ci} = \frac{1}{\sqrt{1+r_i^2}}(s_i + \mathbf{r}_i\cdot\mathbf{p}_i), \tag{5}$$

with the variational parameters $\mathbf{r}_i$ chosen such that the condensate state gives the minimum expectation value of the Hamiltonian in the large-N limit.

The condensate bosons allow us to study the geometry of a bent molecule since the vectors $\mathbf{r}_1, \mathbf{r}_2$ are assumed to give the directions of the two bonds carrying the U(4) groups. We take the angle between the two bonds of the molecule to be equal to the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$.

Due to the rotational invariance of the Hamiltonian, its expectation value in the condensate state only depends on the lengths of $\mathbf{r}_1$ and $\mathbf{r}_2$ and the angle θ between them. In the large-N limit the energy of the condensate is given by

$$\begin{aligned}E(r_1,r_2,\theta) = {}& 4A_1\frac{r_1^2}{(1+r_1^2)^2}N_1^2 + 4A_2\frac{r_2^2}{(1+r_2^2)^2}N_2^2 + 4A_{12}\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{(1+r_1^2)(1+r_2^2)}N_1N_2 \\ &+\lambda\frac{r_1^2+r_2^2-2\mathbf{r}_1\cdot\mathbf{r}_2}{(1+r_1^2)(1+r_2^2)}N_1N_2 + \mu\frac{(\mathbf{r}_1\times\mathbf{r}_2)^2}{(1+r_1^2)(1+r_2^2)}N_1N_2 \\ &+h_1\frac{r_1^4}{(1+r_1^2)^2}N_1^2 + h_2\frac{r_2^4}{(1+r_2^2)^2}N_2^2 + h_{12}\frac{r_1^2r_2^2}{(1+r_1^2)(1+r_2^2)}N_1N_2. \end{aligned} \tag{6}$$

The variational parameters r_1, r_2 and θ can be determined from the extremum conditions

$$\frac{\partial E(r_1,r_2,\theta)}{\partial r_i} = 0, \quad \frac{\partial E(r_1,r_2,\theta)}{\partial \theta} = 0. \tag{7}$$

The condensate is now used as a starting point to construct the harmonic vibrations of the molecule. The RPA induces correlations in the ground-state wave functions [16], but these have no effect on energy differences, and hence we do not consider them further. Vibrational excitations and rotational zero modes are described by fluctuation bosons that are orthogonal to the condensate bosons. Let us choose the coordinates so that the x-z plane coincides with the molecular plane and that $\mathbf{r}_i$ makes an angle ϕ_i with the positive z axis with $\phi_1 = -\frac{\theta}{2}$ and $\phi_2 = \frac{\theta}{2}$; see Fig. 1. The molecular bond angle is θ. In this coordinate system, the condensate bosons are given by

$$b_{ic} = \frac{1}{\sqrt{1+r_i^2}}(s_i + r_i\cos\phi_i p_{iz} + r_i\sin\phi_i p_{ix}). \tag{8}$$

The fluctuation bosons should be orthogonal to the condensate bosons, as well as to each other. A convenient choice is

$$b_{i\alpha} = \frac{1}{\sqrt{1+r_i^2}}(-r_is_i + \cos\phi_i p_{iz} + \sin\phi_i p_{ix}), \tag{9}$$

$$b_{i\beta} = -\sin\phi_i p_{iz} + \cos\phi_i p_{ix}, \tag{10}$$

$$b_{i\gamma} = p_{iy}. \tag{11}$$

The geometrical meaning of these fluctuation bosons was explored in I where we found that $b_{i\alpha}$ boson describes stretching of each bond and $b_{i\beta}$ and $b_{i\gamma}$ describes its rotations. Linear combinations of $b_{1\beta}$ and $b_{2\beta}$ correspond to bending as well as rotations around the y axis of the whole molecule.

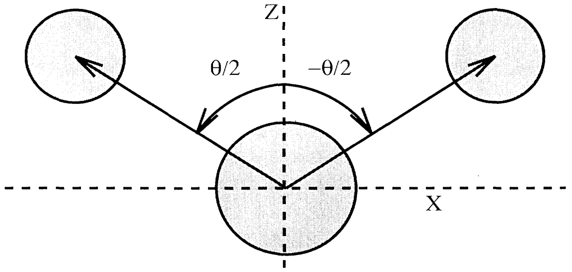

FIG. 1. A schematic depiction of the coordinates used in this work. The molecular plane coincides with the x-z plane, and the bond vectors make an angle $\pm\theta/2$ with the z axis.

The MFA Hamiltonian which gives the large-N harmonic spectra can be obtained in a straightforward way with the aid of the condensate and fluctuation bosons. We first express s_i and $\mathbf{p}_i$ bosons in terms of the condensate and fluctuation bosons and rewrite the Hamiltonian. We then make the substitution

$$b_{ic}^\dagger b_{ic} \rightarrow N_i - b_{i\alpha}^\dagger b_{i\alpha} - b_{i\beta}^\dagger b_{i\beta} - b_{i\gamma}^\dagger b_{i\gamma} \tag{12}$$

as often as possible. After this, we use the Bogoliubov prescription

$$b_{ic}^\dagger = \sqrt{N_i}, \quad b_{ic} = \sqrt{N_i}, \quad i = 1, 2, \tag{13}$$

and neglect the terms with three or more fluctuation bosons. Terms linear in fluctuation bosons vanish due to the extremum condition. Terms that are quadratic in fluctuation bosons constitute the MFA Hamiltonian and constant terms give the expectation value of the Hamiltonian in the condensate state. This procedure is the large-boson number form of the RPA, and correctly reproduces the zero modes.

III. VIBRON MODEL FOR X_2Y: ANALYTICAL SOLUTION

It is much easier to analyze the MFA Hamiltonian expressed in terms of the fluctuation bosons than the original Hamiltonian since the fluctuation bosons become just a set of coupled harmonic oscillators in the mean-field limit. Normal mode frequencies can be found by a simple diagonalization of the RPA matrices, which can be read off from the MFA Hamiltonian, as we showed in I. To further simplify the discussion, we specialize this section to study bent X_2Y molecules for which we can obtain analytical solutions in the MFA with the aid of the C_{2v} symmetry of these molecules [15]. We choose the identical XY bonds to be the carriers of the U(4) groups and because of the point group symmetry we can set $A_1 = A_2 = A, h_1 = h_2 = h, B_1 = B_2 = B, N_1 = N_2 = N$, and $r_1 = r_2 = r$ in the following.

A. Energy spectra

For bent X_2Y molecules, the extremum conditions (7) become

$$[4A + 2A_{12}\cos\theta + \lambda(1-\cos\theta)](1-r^2) + 2hr^2 + h_{12}r^2 + \mu r^2 \sin^2\theta = 0 \quad (14)$$

and

$$\sin\theta(-2A_{12} + \lambda + \mu r^2 \cos\theta) = 0. \quad (15)$$

From these equations, we can solve for the condensate parameters r and θ. As we can see, if $h = h_{12} = 0$, there is a solution with $\theta = 0$ (or π) and $r = 1$ which corresponds to a linear molecule. Therefore, the U(3) terms ($h \neq 0, h_{12} \neq 0$) are essential for bent geometry.

The MFA Hamiltonian for a bent X_2Y molecule is

$$\frac{1}{N} H_{\mathrm{MFA}} = H_{1,1} + H_{2,0} + H_{0,2}, \quad (16)$$

where

$$\begin{aligned}
H_{1,1} = {} & \frac{1}{(1+r^2)^2}[\, 2A(1-r^2)^2 - 4r^2\cos\theta A_{12} + (2r^2\cos\theta + 1 - r^2)\lambda \\
& + \mu(r^2\cos^2\theta + r^4\cos 2\theta) + 2hr^2 + h_{12}r^2 + 2Br^2(1+r^2)](b^\dagger_{1\beta}b_{1\beta} + b^\dagger_{2\beta}b_{2\beta}) \\
& + \frac{1}{1+r^2}\left[A_{12}(r^2+\cos\theta) - \lambda\cos\theta - \mu r^2\cos^2\theta + r^2 B_{12}\right](b^\dagger_{1\beta}b_{2\beta} + b_{1\beta}b^\dagger_{2\beta}) \\
& + \frac{1}{(1+r^2)^2}\left[-16r^2A + 2(1-r^2)^2A - 8r^2\cos\theta A_{12} + (1 + 4r^2\cos\theta - 2r^2 + r^4)\lambda \right. \\
& \qquad \left. + r^2(1-r^2)\sin^2\theta\mu + 2hr^2(2-r^2) + h_{12}r^2(1-r^2)\right](b^\dagger_{1\alpha}b_{1\alpha} + b^\dagger_{2\alpha}b_{2\alpha}) \\
& + \frac{1}{(1+r^2)^2}\left[(1-r^2)^2\cos\theta A_{12} - (\cos\theta + 2r^2 + r^4\cos\theta)\lambda + r^2\sin^2\theta\mu + h_{12}r^2\right](b^\dagger_{1\alpha}b_{2\alpha} + b^\dagger_{2\alpha}b_{1\alpha}) \\
& + \frac{\sin\theta}{(1+r^2)^{3/2}}\left[-2r^2A_{12} + r^2\lambda - r^2\cos\theta\mu\right](b^\dagger_{1\beta}b_{1\alpha} + b^\dagger_{1\alpha}b_{1\beta} - b^\dagger_{2\beta}b_{2\alpha} - b^\dagger_{2\alpha}b_{2\beta}) \\
& + \frac{\sin\theta}{(1+r^2)^{3/2}}\left[(1-r^2)A_{12} - \lambda - r^2\cos\theta\mu\right](b^\dagger_{1\beta}b_{2\alpha} + b^\dagger_{2\alpha}b_{1\beta} - b^\dagger_{2\beta}b_{1\alpha} - b^\dagger_{1\alpha}b_{2\beta}) \\
& + \left[A\frac{2-8r^2}{(1+r^2)^2} + 2(A+B)\frac{r^2}{1+r^2} + (2h+h_{12})\frac{r^2}{(1+r^2)^2} - A_{12}\frac{4r^2\cos\theta}{(1+r^2)^2}\right. \\
& \qquad \left. + \lambda\frac{1 - r^2 + 2r^2\cos\theta}{(1+r^2)^2} + \mu\frac{r^2(1+r^2\cos\theta)}{(1+r^2)^2}\right](b^\dagger_{1\gamma}b_{1\gamma} + b^\dagger_{2\gamma}b_{2\gamma}) \\
& + \left[(A_{12}+B_{12})\frac{r^2\cos\theta}{1+r^2} + A_{12}\frac{1}{1+r^2} - \lambda\frac{1}{1+r^2} - \mu\frac{r^2\cos\theta}{1+r^2}\right](b^\dagger_{1\gamma}b_{2\gamma} + b^\dagger_{2\gamma}b_{1\gamma})
\end{aligned} \quad (17)$$

and

$$\begin{aligned}
H_{2,0} + H_{0,2} = {} & \left[A\frac{1-r^2}{1+r^2} - B\frac{r^2}{1+r^2}\right]\left[(b^\dagger_{1\beta})^2 + b^2_{1\beta} + (b^\dagger_{2\beta})^2 + b^2_{2\beta}\right] \\
& + \frac{1}{1+r^2}\left[A_{12}(\cos\theta - r^2) + \mu r^2\sin^2\theta - B_{12}r^2\right](b_{1\beta}b_{2\beta} + b^\dagger_{1\beta}b^\dagger_{2\beta}) \\
& + \frac{\sin\theta}{(1+r^2)^{3/2}}\left[A_{12}(1-r^2) + \lambda r^2 - \mu r^2\cos\theta\right](b_{1\beta}b_{2\alpha} + b^\dagger_{1\beta}b^\dagger_{2\alpha} - b_{2\beta}b_{1\alpha} - b^\dagger_{2\beta}b^\dagger_{1\alpha}) \\
& + \frac{1}{(1+r^2)^2}\left[A(1-r^2)^2 + hr^2\right]\left[(b^\dagger_{1\alpha})^2 + b^2_{1\alpha} + (b^\dagger_{2\alpha})^2 + b^2_{2\alpha}\right] \\
& + \frac{1}{(1+r^2)^2}\left[A_{12}(1-r^2)^2\cos\theta + \lambda 2r^2(\cos\theta - 1) + \mu r^2\sin^2\theta + h_{12}r^2\right](b_{1\alpha}b_{2\alpha} + b^\dagger_{1\alpha}b^\dagger_{2\alpha}) \\
& + \left[A\frac{1}{1+r^2} - (A+B)\frac{r^2}{1+r^2}\right]\left[(b^\dagger_{1\gamma})^2 + b^2_{1\gamma} + (b^\dagger_{2\gamma})^2 + b^2_{2\gamma}\right] \\
& + \left[-(A_{12}+B_{12})\frac{r^2\cos\theta}{1+r^2} + A_{12}\frac{1}{1+r^2}\right]\left[b^\dagger_{1\gamma}b^\dagger_{2\gamma} + b_{1\gamma}b_{2\gamma}\right].
\end{aligned} \quad (18)$$

We have divided the Hamiltonian H_{MFA} by the constant scaling factor N for convenience. If we define a fluctuation boson number operator $N_f = \sum_{i=1,2}(b^\dagger_{i\alpha}b_{i\alpha} + b^\dagger_{i\beta}b_{i\beta} + b^\dagger_{i\gamma}b_{i\gamma})$, it is easy to see that $H_{1,1}$ conserves the fluctuation boson number while $H_{2,0} + H_{0,2}$ do not. Note that although these expressions are long, all terms are quadratic in the fluctuation bosons and hence the full expression simply describes a set of coupled oscillators.

The solution of the MFA Hamiltonian given by Eqs. (16)–(18) is standard and it is well known [16] that such a quadratic boson Hamiltonian can always be reduced to the following form with intrinsic normal modes separated from collective zero modes:

$$H = \sum_i \omega_i O_i^\dagger O_i + \sum_i \frac{L_i^2}{2I_i}. \tag{19}$$

Here $O_i^\dagger$ are normal-mode boson operators with energies ω_i and L_i are Hermitian collective zero-mode operators with I_i the corresponding moments of inertia. Approximate forms for the moments of inertia have been given in the nuclear physics literature [16] (the Inglis and Thouless-Valatin forms). These expressions can be derived from the RPA ones under suitable approximations [16].

The corresponding RPA ground state is the vacuum for O_i, i.e., $O_i\,|0\rangle_{\mathrm{RPA}} = 0$ for all i. For bent X_2Y molecules, there are three normal modes and three zero modes. The normal modes are vibrational motions in the molecular plane. They are constructed from the corresponding local modes that are shown in Fig. 2: symmetric stretching, antisymmetric stretching, and bending. They transform under the point group C_{2v} as the representations A_1, B_2 and A_1, respectively [15]. The zero modes correspond to rotations of the whole molecule generated by the components of the angular momentum operator

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2. \tag{20}$$

The rotations generated by L_x and L_z rotate the molecule about axes in its plane, while that generated by L_y rotates it about the axis perpendicular to that plane. Like the antisymmetric stretching mode, L_y transforms as B_2. The MFA Hamiltonian can thus be decomposed into three disjoint pieces for (i) symmetric stretching and bending; (ii) antisymmetric stretching and rotation around y axis; and (iii) rotations around x and z axes.

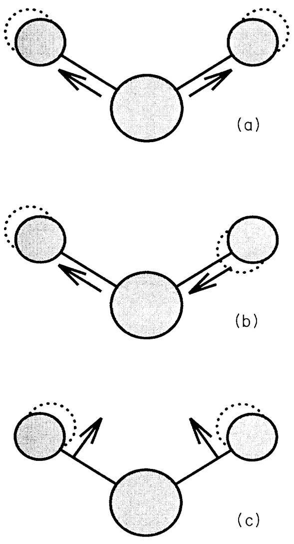

FIG. 2. The geometric content of the local modes: A depicts the symmetric stretching mode, B the antisymmetric stretching mode, and finally C the bending mode.

From the geometrical meaning of the fluctuation bosons, we can easily construct new boson operators for the vibrational motions that have definite C_{2v} symmetries. We have, for the local-mode symmetric stretching,

$$b_s = \frac{1}{\sqrt{2}}(b_{1\alpha} + b_{2\alpha}), \tag{21}$$

for the local antisymmetric stretching mode,

$$b_a = \frac{1}{\sqrt{2}}(b_{1\alpha} - b_{2\alpha}), \tag{22}$$

and for the local bending mode,

$$b_b = \frac{1}{\sqrt{2}}(b_{1\beta} - b_{2\beta}). \tag{23}$$

The zero-mode operators are given by the angular momentum operators. Using the Bogoliubov prescription (13) for condensate bosons and taking the leading terms in large N, we can express them as a linear combination of the fluctuation bosons

$$\begin{aligned} L_x &= i\frac{r\sqrt{N}}{\sqrt{1+r^2}}\cos\frac{\theta}{2}(b_{1\gamma} - b_{1\gamma}^\dagger + b_{2\gamma} - b_{2\gamma}^\dagger), \\ L_y &= -i\frac{r\sqrt{N}}{\sqrt{1+r^2}}(b_{1\beta} - b_{1\beta}^\dagger + b_{2\beta} - b_{2\beta}^\dagger), \\ L_z &= i\frac{r\sqrt{N}}{\sqrt{1+r^2}}\sin\frac{\theta}{2}(b_{1\gamma} - b_{1\gamma}^\dagger - b_{2\gamma} + b_{2\gamma}^\dagger). \end{aligned} \tag{24}$$

Our objective is to rewrite the MFA Hamiltonian in terms of these new boson operators and zero-mode operators. For convenience we introduce the scaled operator

$$l_y = -\frac{i}{2}(b_{1\beta} + b_{2\beta} - b_{1\beta}^\dagger - b_{2\beta}^\dagger) \tag{25}$$

instead of L_y and we also introduce the canonically conjugate angle

$$\phi_y = \frac{1}{2}(b_{1\beta} + b_{2\beta} + b_{1\beta}^\dagger + b_{2\beta}^\dagger). \tag{26}$$

Expressing the fluctuation boson operators in terms of these new boson and zero-mode operators, we find that indeed the MFA Hamiltonian becomes a sum of three disjoint pieces as we expected:

$$\frac{1}{N}H_{\mathrm{MFA}} = H_1 + H_2 + H_3, \tag{27}$$

where

$$\begin{aligned} H_1 = {} & A_{bb}b_b^\dagger b_b + A_{ss}b_s^\dagger b_s + A_{bs}(b_b^\dagger b_s + b_s^\dagger b_b) \\ & + B_{bb}(b_b^2 + b_b^{\dagger 2}) + B_{ss}(b_s^2 + b_s^{\dagger 2}) \\ & + B_{bs}(b_b b_s + b_b^\dagger b_s^\dagger), \end{aligned} \tag{28}$$

$$H_2 = A_{aa}b_a^\dagger b_a + B_{aa}(b_a^2 + b_a^{\dagger 2}) + iD_o l_y(b_a - b_a^\dagger) - D_t l_y^2, \tag{29}$$

and

$$\begin{aligned} H_3 = {} & \frac{A(1-r^2)-Br^2}{1+r^2}\left[(b_{1\gamma}^\dagger - b_{1\gamma})^2 + (b_{2\gamma}^\dagger - b_{2\gamma})^2\right] \\ & + \frac{A_{12}(1-r^2\cos\theta)-B_{12}r^2\cos\theta}{1+r^2} \\ & \times (b_{1\gamma}^\dagger - b_{1\gamma})(b_{2\gamma}^\dagger - b_{2\gamma}). \end{aligned} \tag{30}$$

H_1 mixes the local symmetric stretching mode and bending mode, H_2 mixes the local antisymmetric stretching mode and rotations about the y axis, and H_3 contains only rotations about the x and z axes. The expressions for the coefficients appearing in (28) and (29) are rather lengthy, and can be found in Appendix B. It should be pointed out that in arriving at (30), we have used the extremum conditions. It is also interesting to note the fact that the contribution of the angle ϕ_y, conjugate to l_y, vanishes because l_y corresponds to a zero mode.

The solution of the MFA Hamiltonian (16) is now straightforward. We start with H_1 given by (28) which can be diagonalized to give the uncoupled symmetric stretching and bending normal modes, generated by the operators $O_s^\dagger$ and $O_b^\dagger$:

$$\begin{aligned} O_b^\dagger &= X_{11}b_b^\dagger + X_{12}b_s^\dagger - Y_{11}b_b - Y_{12}b_s, \\ O_s^\dagger &= X_{21}b_b^\dagger + X_{22}b_s^\dagger - Y_{21}b_b - Y_{22}b_s. \end{aligned} \tag{31}$$

The row vectors in the X and Y matrices satisfy the RPA equations [16]

$$\begin{aligned} \mathcal{A}X_n + \mathcal{B}Y_n &= \omega_n X_n, \\ \mathcal{B}X_n + \mathcal{A}Y_n &= -\omega_n Y_n, \end{aligned} \tag{32}$$

and obey the normalization condition

$$\sum_i (X_{ni}X_{mi} - Y_{ni}Y_{mi}) = \delta_{nm}. \tag{33}$$

The RPA matrices $\mathcal{A}$ and $\mathcal{B}$ are given by

$$\mathcal{A} = \begin{pmatrix} A_{bb} & A_{bs} \\ A_{bs} & A_{ss} \end{pmatrix}, \quad \mathcal{B} = \begin{pmatrix} 2B_{bb} & B_{bs} \\ B_{bs} & 2B_{ss} \end{pmatrix}. \tag{34}$$

Since these are two by two matrices, we can solve (32) and (33) analytically. If we introduce the notation

$$\begin{aligned} \Delta_1 &= A_{bb}^2 - 4B_{bb}^2 + A_{bs}^2 - B_{bs}^2, \\ \Delta_2 &= A_{ss}^2 - 4B_{ss}^2 + A_{bs}^2 - B_{bs}^2, \\ f_1 &= (A_{bb} - 2B_{bb})(A_{bs} + B_{bs}) \\ &\quad + (A_{ss} + 2B_{ss})(A_{bs} - B_{bs}), \\ f_2 &= (A_{bb} + 2B_{bb})(A_{bs} - B_{bs}) \\ &\quad + (A_{ss} - 2B_{ss})(A_{bs} + B_{bs}), \end{aligned} \tag{35}$$

we find that the normal-mode bending frequency ω_b is given by

$$\omega_b^2 = \frac{1}{2}(\Delta_1 + \Delta_2) - \frac{1}{2}\sqrt{(\Delta_1 - \Delta_2)^2 + 4f_1f_2}, \tag{36}$$

and that the normal-mode symmetric stretching frequency ω_s is

$$\omega_s^2 = \frac{1}{2}(\Delta_1 + \Delta_2) + \frac{1}{2}\sqrt{(\Delta_1 - \Delta_2)^2 + 4f_1f_2}. \tag{37}$$

A word of caution is in order here. In order for the solution given by (36) and (37) to be physically acceptable, we must require that the matrices $(\mathcal{A}-\mathcal{B})$ and $(\mathcal{A}+\mathcal{B})$ be both positive definite. This corresponds to requiring that locally both the mass parameter and second derivative of potential energy be positive definite.

The solution of H_2 given by (29) involves making a shift of the b_a boson along the zero-mode motion,

$$g = b_a + xl_y \tag{38}$$

and

$$g^\dagger = b_a^\dagger - xl_y. \tag{39}$$

It is easy to see that g obeys boson commutation relations. We can decouple g and l_y by taking $x = iD_0/(2B_{aa} - A_{aa})$ and we get

$$H_2 = A_{aa}g^\dagger g + B_{aa}(g^{\dagger 2} + g^2) - Dl_y^2, \tag{40}$$

where

$$D = D_t - D_0^2/(2B_{aa} - A_{aa}). \tag{41}$$

In the form of (40) H_2 can be reduced to a normal-mode form by a Bogoliubov transformation

$$\begin{aligned} g &= \cosh\psi O_a + \sinh\psi O_a^\dagger, \\ g^\dagger &= \cosh\psi O_a^\dagger + \sinh\psi O_a. \end{aligned} \tag{42}$$

We find from the requirement that O_a and the zero mode be decoupled that $\sinh 2\psi = -2B_{aa}/\omega_a, \cosh 2\psi = A_{aa}/\omega_a$. We also use $L_y^2 = \frac{4r^2N}{1+r^2}l_y^2$ and obtain

$$H_2 = \omega_a O_a^\dagger O_a + \frac{L_y^2}{2I_y}. \tag{43}$$

The normal-mode frequency for the asymmetric stretching mode is

$$\omega_a = \sqrt{A_{aa}^2 - 4B_{aa}^2}, \tag{44}$$

and the moment of inertia around y axis is

$$I_y = -\frac{2r^2N\hbar^2}{(1+r^2)D}. \tag{45}$$

In order for H_2 to have a physical solution, we must require $A_{aa}^2 - 4B_{aa}^2 > 0$.

The final term in (27), H_3, involves only rotations and we can readily show that this can be brought to the form

$$H_3 = \frac{L_x^2}{2I_x} + \frac{L_z^2}{2I_z}. \tag{46}$$

The moments of inertia are given by

$$I_x = -\frac{2r^2\cos^2\frac{\theta}{2}N\hbar^2}{[2A(1-r^2)-2Br^2+A_{12}(1-r^2\cos\theta)-B_{12}r^2\cos\theta]} \tag{47}$$

and

$$I_z = -\frac{2r^2\sin^2\frac{\theta}{2}N\hbar^2}{[2A(1-r^2)-2Br^2-A_{12}(1-r^2\cos\theta)+B_{12}r^2\cos\theta]}\,. \tag{48}$$

Thus we have seen that in MFA the Hamiltonian we have taken including the Casimir operators of the U(3) subgroups naturally describes a bent symmetric molecule with the expected bending mode, two stretching modes, and three zero modes.

B. Transitions

Transition intensities provide additional information about the structure of molecules. As discussed in I, since wave functions of the molecules are needed in calculating transition intensities and since in MFA they are only accurate to the order $\frac{1}{\sqrt{N}}$, we have to limit the use of the MFA to transitions with few quanta. For bent X_2Y molecules, the most important vibrational transitions are usually dipole transitions. Since we wish to study the constraint imposed by the transition measurements on the parameters in the Hamiltonian, we use a simple dipole operator and calculate in the MFA only transitions from the ground state to three fundamental vibrational excitations. We take the dipole operator of the bent X_2Y to be the sum

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2, \tag{49}$$

where T_1 and T_2 are the dipole operators for the two bonds and as in I, they are given by

$$\mathbf{T}_i = \gamma_0\mathbf{D}_i + \gamma_1^{'}(\mathbf{D}_i e^{-\lambda n_{pi}} + e^{-\lambda n_{pi}}\mathbf{D}_i), \quad i = 1, 2. \tag{50}$$

This is a very special form of the general dipole operator expansion in terms of the generators of $\mathrm{U}_1(4) \times \mathrm{U}_2(4)$ suggested in [5]. We not only neglect the coupling effect for each $\mathbf{T}_i$ but also choose $\mathbf{T}$ to be symmetric as is appropriate for symmetric molecules (contrast Ref. [5]).

In the MFA, we obtain for the static dipole moment

$$T = (\gamma_0+\gamma_1)\frac{4rN}{1+r^2}\cos\frac{\theta}{2}, \tag{51}$$

with $\gamma_1 = \gamma_1^{'} e^{-\frac{\lambda r^2 N}{1+r^2}}$. The transition dipole operator is

$$\begin{aligned} T_x = {} & \xi\,\cos\frac{\theta}{2}(b_{1\beta}+b_{1\beta}^\dagger+b_{2\beta}+b_{2\beta}^\dagger) \\ & -\eta\sin\frac{\theta}{2}(b_{1\alpha}+b_{1\alpha}^\dagger-b_{2\alpha}-b_{2\alpha}^\dagger), \end{aligned} \tag{52}$$

$$\begin{aligned} T_z = {} & \xi\,\sin\frac{\theta}{2}(b_{1\beta}+b_{1\beta}^\dagger-b_{2\beta}-b_{2\beta}^\dagger) \\ & +\eta\cos\frac{\theta}{2}(b_{1\alpha}+b_{1\alpha}^\dagger+b_{2\alpha}+b_{2\alpha}^\dagger), \end{aligned} \tag{53}$$

where

$$\begin{aligned} \xi &= (\gamma_0+\gamma_1)\sqrt{\frac{N}{1+r^2}}, \\ \eta &= \left[(\gamma_0+\gamma_1)\frac{1-r^2}{1+r^2} - \gamma_1\frac{2\lambda r^2 N}{(1+r^2)^2}\right]\sqrt{N}. \end{aligned} \tag{54}$$

Since T_y involves only zero-mode operators and does not contribute to transitions from the ground state to any normal-mode excitations, we will not consider it. It is interesting to note that although there are three parameters for the dipole operator in (49) and (50), its mean-field limit involves only ξ and η, which are two independent combinations of these parameters. The transition intensities are given by

$$I_{(0)\to(v)} = \frac{8\pi^3}{3hc}\omega|\,\langle v|\,\mathbf{T}\,|0\rangle\,|^2, \tag{55}$$

where (0) is the ground state and $(v) = (v_1v_2v_3)$ is the excited vibrational state. We only consider the three fundamental vibrational states for (v). In terms of the normal-mode operators obtained in Sec. III A, we can write them as

$$\begin{aligned} |s\rangle &= O_s^\dagger\,|0\rangle\,, \\ |a\rangle &= O_a^\dagger\,|0\rangle\,, \\ |b\rangle &= O_b^\dagger\,|0\rangle\,. \end{aligned} \tag{56}$$

We can calculate easily the transition matrix elements of the dipole operator between the ground-state and normal-mode states in the MFA by using (52) and (53). We find for the symmetric stretching mode

$$\langle s|\,T_x\,|0\rangle = 0, \tag{57}$$

$$\begin{aligned} \langle s|\,T_z\,|0\rangle = {} & \eta\sqrt{2}\cos\frac{\theta}{2}(X_{22}+Y_{22}) \\ & +\xi\sqrt{2}\sin\frac{\theta}{2}(X_{21}+Y_{21}), \end{aligned} \tag{58}$$

for the antisymmetric stretching mode,

$$\langle a|\,T_x\,|0\rangle = -\sqrt{2}\eta\sin\frac{\theta}{2}(\sinh\psi+\cosh\psi), \tag{59}$$

$$\langle a|\,T_z\,|0\rangle = 0, \tag{60}$$

and finally for the bending mode,

$$\langle b|\,T_x\,|0\rangle = 0, \tag{61}$$

$$\begin{aligned} \langle b|\,T_z\,|0\rangle = {} & \eta\sqrt{2}\cos\frac{\theta}{2}(X_{12}+Y_{12}) \\ & +\xi\sqrt{2}\sin\frac{\theta}{2}(X_{11}+Y_{11}). \end{aligned} \tag{62}$$

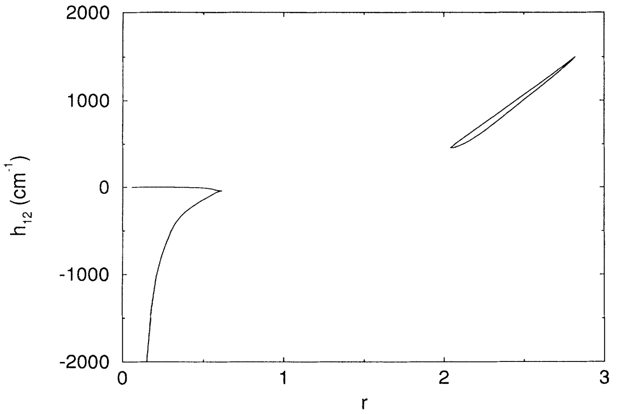

FIG. 3. The result of fitting the harmonic energies and moments of inertia to the Hamiltonian of Eq. (16). We show only h_{12} as a function of the dimensionless parameter r.

IV. APPLICATION: WATER MOLECULE

We want to demonstrate the usefulness of the Hamiltonian (3) suggested in Sec. II for bent molecules and of its treatment in MFA by studying the water molecule. Specifically we want to construct a Hamiltonian that reproduces the harmonic vibrational energies, the moments of inertia for the rotational motion of the molecule, as well as its transition properties using the analytical solution we obtained in the preceding section. We do not intend to seek a detailed fit to the entire energy spectrum of the water molecule. Such a description not only requires the exact diagonalization of the Hamiltonian but also needs higher-order terms in the expansion of the Hamiltonian in the $U_1(4) \times U_2(4)$ generators. An approximate treatment is useful because it provides a starting point for such a more complex calculation, because it gives geometric insight to the vibron model approach applied to water, and because it yields a dynamically sound but relatively simple starting point for the discussion of processes like electron scattering.

We associate the two U(4) groups with the identical HO bonds. The number of bosons for each U(4) group is fixed by counting the number of vibrational levels in the diatomic molecule HO, as explained in [5]. That gives $N = 39$. There are eight parameters in the Hamiltonian (3) for a symmetric bent molecule: $A, A_{12}, \lambda, \mu, h, h_{12}, B$, and B_{12}. One of them can be eliminated since the Hamiltonian is constrained to reproduce the bond angle between the two bonds. The experimental value of this angle is $\theta = 105°$. We are thus left with seven independent parameters.

We start with constructing Hamiltonians that yield the vibrational normal modes and the moments of inertia of the water molecule, all of which have been measured experimentally. Since there are three normal modes and three moments of inertia, we expect these Hamiltonians to map out one or several one-dimensional paths in the seven-dimensional parameter space. Let us use h_{12} as a function of r to parametrize these paths. Indeed we have found such paths in the range $0.2 < r < 0.6$ and $2.0 < r < 2.6$, as shown in Fig. 3. We have not attempted to locate all possible solutions, however.

Not all Hamiltonians lying on these paths are physically acceptable. Transition intensities contain information about the wave function of the water molecule and therefore impose stringent constraints on the Hamiltonians. There are four experimental quantities we can study in the MFA. They are the static dipole moment and the transition intensities to three fundamental modes. As we see from the result in Sec. III B, our choice of the dipole operator involves only two more parameters in the MFA. Thus the four new quantities overconstrain the fit and it is not obvious that any of the Hamiltonians we obtain by using the spectrum information yield a wave function which reproduces all four dipole quantities, particularly in view of the strong cancellation in the symmetric stretching transition seen in the experiment. We proceed with the selection of Hamiltonian parameters by calculating the dipole transition intensities using the parameter values on the paths we have found above. The calculation shows that a Hamiltonian that gives reasonable fits to the static dipole moment and the transition intensities exists and its parameters are given in Table I. The corresponding parameters for the MFA of the dipole operator are given in Table II. The quality of the fit can be seen in Table III where we compare our results for excitation energies, moments of inertia, and transition rates with experiment and with those of [5]. Note that these authors did not calculate moments of inertia. As we can see, we overestimate the transition intensity for the symmetric stretching mode. This is because the cancellations implied by this weak transition are sensitive to the $1/\sqrt{N}$ corrections which are missing from our mean-field treatment.

V. CONCLUSION

In this paper we have shown that considerable simplification and geometric insight arises from a mean-field approximation to the algebraic or vibron treatment of bent triatomic molecules. The MFA is valid for large boson number, which is the case for these molecules. The MFA makes it particularly easy to see what terms must be added to the molecular Hamiltonian to give a bent molecule in the intrinsic frame. The low-lying vibrational

TABLE I. Parameters (in units of cm^{-1}) for the Hamiltonian (16), obtained by fitting the MFA to the spectrum and transitions of water. They yield a bent condensate with $r = 2.441$ and $\theta = 105°$.

A	A_{12}	λ	μ	h	h_{12}	B	B_{12}
−443.9	246.6	498.5	3.514	−532.3	988.1	392.1	−314.4

TABLE II. Parameters (in units of Å) for the dipole operator, obtained by fitting the MFA to the transitions of water.

η	ξ
0.0038	0.0027

energies, moments of inertia, and vibrational transition rates can then be used to fix the Hamiltonian parameters.

There are many directions that one can take from this work. One can take the MFA Hamiltonian with its harmonic treatment of excitations as an attempt at a more exact treatment. This is far easier than trying to determine the parameters in a full treatment directly. Alternately one can use the MFA Hamiltonian in a calculation of electron-molecule scattering where the fine details of the energies are not nearly so important as the overall molecular dynamics [18]. We plan just such a calculation of electron-water scattering. Finally, and perhaps most importantly, the MFA with its simplicity and geometric base permits extension to more complex polyatomic molecules for which full treatment by conventional or algebraic methods is often far too difficult.

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APPENDIX A: GEOMETRY AND MFA OF THE HAMILTONIAN EQ. (2)

A formalism that may give a unified description of both linear and bent triatomic molecules in the algebraic vibron model was suggested in [3]. The idea is based on a group theoretical solution for the eigenvalues of a simple Hamiltonian, that displays all the properties associated with both linear and bent molecules, depending on the value of a single parameter. The case with exact dynamical symmetry is $\lambda = 0$ in Eq. (2):

$$H = -A_1\hat{C}_1 - A_2\hat{C}_2 - A_{12}\hat{C}_{12}. \qquad \text{(A1)}$$

Here the operators $\hat{C}_1, \hat{C}_2$, and $\hat{C}_{12}$ are defined in (1). It was shown in [3] by calculating the low-lying vibrational excitations from group theory that for any parameter $a \neq 2$ in the operator $\hat{C}_{12}$ one has four normal modes typical of a linear molecule. For $a = 2$ one of the modes becomes a zero mode, so that we see three normal modes that seem to indicate that this case describes a bent molecule. It was found [3] that if $a = 2$, the three normal mode frequencies are $\omega_{s1} = 4(A_1 + 4A_{12})N_1 + 4A_{12}N_2$, $\omega_{s2} = 4(A_2 + 4A_{12})N_2 + 4A_{12}N_1$, and $\omega_b = 4A_{12}(N_1 + N_2)$. To illustrate how the zero mode appears, and why this is not a satisfactory solution, we study the Hamiltonian (A1) in MFA.

It is easy to show that the expectation value of the operators

$$C_2'(\mathrm{O}_{12}(4)) = \mathbf{L} \cdot \mathbf{D} \qquad \text{(A2)}$$

in the condensate given by (3) vanishes, since this expectation value is proportional to the imaginary part of the condensate parameters. For linear molecules we have been able to prove that the condensate is an eigenstate of this operator, with eigenvalue zero, while to leading order in N any condensate is an eigenstate of this operator with eigenvalue zero. Remember that the absolute value of an operator is defined through its spectral decomposition, as having the same eigenvectors as the original operator, replacing the eigenvalues by their absolute value. Any condensate state thus has no contribution from C_2', and thus $|\mathbf{L}\cdot\mathbf{D}|$ does not contribute to the energy surface. Therefore, even though this term was introduced for bent molecules, the Hamiltonian (A1) with any a, and in particular $a = 2$, has an identical energy surface $E(r_1, r_2, \theta)$ as that with $a = 0$. The analysis we presented in Sec. IV A of I for the solution of ground-state condensates of linear molecules can be readily carried over for the case of bent molecules. Since in realistic application one finds the relation $A_{12} > 0$, the condensate has $\theta = 0$ even when $a = 2$. (We also find $r_1 = r_2 = 1$.) The geometries of the condensates of the realistic Hamiltonians used in [5] [see its Eq. (3.11)] are also linear, as can be shown straightforwardly.

With $r_1 = r_2 = 1, \theta = 0$ for the condensate, we can rewrite C_2' in terms of the condensate bosons and fluctuation bosons. Applying the Bogoliubov prescription

TABLE III. Comparison of fits to the spectrum and transitions of water.

Physical quantity	Units	Expt. [17]	Present work	Iachello and Oss [5]
ω_b	cm^{-1}	1595	1595	1595
ω_s	cm^{-1}	3657	3657	3657
ω_a	cm^{-1}	3756	3756	3756
I_x	$\mathrm{g\ cm}^{-1}$	1.928[−40]	1.928[−40]	
I_y	$\mathrm{g\ cm}^{-1}$	3.017[−40]	3.017[−40]	
I_z	$\mathrm{g\ cm}^{-1}$	1.009[−40]	1.009[−40]	
D_0	e Å	0.38	0.38	
$I_{(000)\to(010)}$	cm/molecule	1040	1059	1040
$I_{(000)\to(100)}$	cm/molecule	49.5	292	51.8
$I_{(000)\to(001)}$	cm/molecule	720	709	732.5

(12-13), we find in the leading order

$$C_2' = -i\Big[N_2(b_{1\beta}^\dagger b_{1\gamma} - b_{1\gamma}^\dagger b_{1\beta}) + N_1(b_{2\beta}^\dagger b_{2\gamma} - b_{2\gamma}^\dagger b_{2\beta}) + \sqrt{N_1N_2}(-b_{1\beta}^\dagger b_{2\gamma} + b_{2\gamma}^\dagger b_{1\beta} - b_{2\beta}^\dagger b_{1\gamma} + b_{1\gamma}^\dagger b_{2\beta})\Big]. \tag{A3}$$

This can be easily diagonalized to give

$$C_2' = (N_1 + N_2)(B_-^\dagger B_- - B_+^\dagger B_+), \tag{A4}$$

where the boson operators $B_+^\dagger$ and $B_-^\dagger$ are given by

$$B_-^\dagger = \frac{1}{\sqrt{2(N_1+N_2)}} \times[\sqrt{N_2}b_{1\beta}^\dagger - \sqrt{N_1}b_{2\beta}^\dagger + i(\sqrt{N_2}b_{1\gamma}^\dagger - \sqrt{N_1}b_{2\gamma}^\dagger)] \tag{A5}$$

and

$$B_+^\dagger = \frac{1}{\sqrt{2(N_1+N_2)}} \times[\sqrt{N_2}b_{1\beta}^\dagger - \sqrt{N_1}b_{2\beta}^\dagger - i(\sqrt{N_2}b_{1\gamma}^\dagger - \sqrt{N_1}b_{2\gamma}^\dagger)]. \tag{A6}$$

These boson operators also create the large-N eigenvectors of $C_2(\mathrm{O}_{12})$, the other term in $\hat{C}_{12}$. The RPA eigenvalues of the Hamiltonian without the absolute value are

$$s_1 : 4(A_1 + A_2)N_1 + 4A_{12}N_2, \tag{A7}$$

$$s_2 : 4(A_1 + A_2)N_2 + 4A_{12}N_1, \tag{A8}$$

$$B_- : A_{12}(2-a)(N_1+N_2), \tag{A9}$$

$$B_+ : A_{12}(2+a)(N_1+N_2), \tag{A10}$$

$$B_- + B_+ : 4A_{12}(N_1+N_2). \tag{A11}$$

The last energy (A10) is not independent, since it is just a double excitation, but its significance will become clear when we take the absolute value. The four independent modes are still the modes of a linear triatomic molecule. The first two are the usual stretching modes. The other two are no longer the degenerate bending modes but rather a linear combination of bending modes corresponding to left and right twists. The are not degenerate because the Hamiltonian violates parity invariance. If we take the absolute value the only thing that changes is the frequency for B_+, which becomes equal to the one for B_- ($a \to -a$). Thus the bending modes are again degenerate as parity has been restored. Notice that now, however, the double excitation is no longer the sum of what used to be its building blocks. It thus seems that we have created five modes, a pair of which is degenerate. Actually one can show, through boson mapping techniques [19], that we have only four operators and one signature quantum number (+/−). The bending mode can be interpreted as the elementary excitation of a composite boson, whereas there are some complicated objects giving the individual + and − excitations. Even for the case of $a = 2$, where we have but three normal (nonzero energy) modes we find that the generators of this extra zero mode are quite complicated. For a true zero mode associated with the breaking of rotational invariance due to the molecular bend, this generator should be an angular momentum, as in Sec. II. It is not here. Thus the "zero mode" generated by taking $a = 2$ is of interesting dynamical character, but does not correspond to the geometrical zero modes of a bent molecule. Even though the discussion in this appendix was limited to a very simple Hamiltonian, realistic Hamiltonians for bent molecules as used in (3.11) of [5] contain the same operators, as well as additional terms involving the Majorana operator. If we add the Majorana term to (A1), we find that for $a = 2$, there should be two degenerate (nonzero energy) harmonic modes for the $B_\pm^\dagger$ bosons due to the contribution from the Majorana operator. This makes it even more difficult to interpret bent molecules in terms of Hamiltonians constructed based on (2).

APPENDIX B: MFA HAMILTONIAN COEFFICIENTS

The coefficients in the MFA Hamiltonians (28) and (29) are given by

$$\begin{aligned}(1+r^2)^2A_{bb} = {} & 2A(1-r^2)^2 - [(1+5r^2)\cos\theta + r^2(1+r^2)]A_{12} + [1 - r^2 + (1+3r^2)\cos\theta]\lambda \\ & +(2r^2\cos^2\theta + r^4\cos 2\theta + r^4\cos^2\theta)\mu + 2hr^2 + h_{12}r^2 + (2B - B_{12})r^2(1+r^2),\end{aligned} \tag{B1}$$

$$\begin{aligned}(1+r^2)^2A_{ss} = {} & 2(1-10r^2+r^4)A + (1-10r^2+r^4)\cos\theta A_{12} \\ & +(1-\cos\theta - 4r^2 + 4r^2\cos\theta + r^4 - r^4\cos\theta)\lambda + (\mu\sin^2\theta + 2h + h_{12})r^2(2-r^2),\end{aligned} \tag{B2}$$

$$\begin{aligned}(1+r^2)^2A_{aa} = {} & 2(1-10r^2+r^4)A - (1+6r^2+r^4)\cos\theta A_{12} \\ & +(1 + 4r^2\cos\theta + r^4 + \cos\theta + r^4\cos\theta)\lambda - r^4\sin^2\theta\mu + 2hr^2(2-r^2) - h_{12}r^4,\end{aligned} \tag{B3}$$

$$A_{bs} = \frac{\sin\theta}{(1+r^2)^{3/2}}[(1-3r^2)A_{12} - (1-r^2)\lambda - 2r^2\cos\theta\mu], \tag{B4}$$

$$B_{bb} = \frac{1}{1+r^2}[(1-r^2)A - r^2B - \tfrac{1}{2}A_{12}(\cos\theta - r^2) - \tfrac{1}{2}\mu r^2\sin^2\theta + \tfrac{1}{2}B_{12}r^2], \tag{B5}$$

$$2B_{ss}(1+r^2)^2 = 2A(1-r^2)^2 + 2hr^2 + h_{12}r^2 + A_{12}(1-r^2)^2\cos\theta + 2\lambda r^2(\cos\theta - 1) + \mu r^2\sin^2\theta, \tag{B6}$$

$$2B_{aa}(1+r^2)^2 = 2A(1-r^2)^2 + 2hr^2 - h_{12}r^2 - A_{12}(1-r^2)^2\cos\theta - 2\lambda r^2(\cos\theta - 1) - \mu r^2\sin^2\theta, \tag{B7}$$

$$B_{bs} = \frac{\sin\theta}{(1+r^2)^{3/2}}[A_{12}(1-r^2) + \lambda r^2 - \mu r^2\cos\theta], \tag{B8}$$

$$\sqrt{2}D_0 = \frac{\sin\theta}{(1+r^2)^{3/2}}[2r^2A_{12} - (1+2r^2)\lambda + \mu r^2\cos\theta], \tag{B9}$$

$$\begin{aligned} 2D_t(1+r^2)^2 = {} & 4Ar^2(1-r^2) - 4Br^2(1+r^2) + 2A_{12}r^2(2\cos\theta - 1 - r^2) \\ & + \lambda(1-r^2)(\cos\theta - 1) + \mu r^2\sin^2\theta(1+2r^2) - 2hr^2 - h_{12}r^2 - 2B_{12}r^2(1+r^2). \end{aligned} \tag{B10}$$

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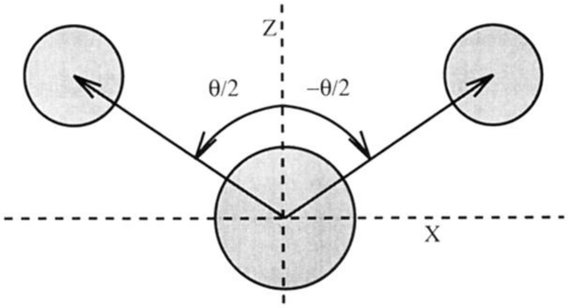

FIG. 1. A schematic depiction of the coordinates used in this work. The molecular plane coincides with the x-z plane, and the bond vectors make an angle $\pm\theta/2$ with the z axis.

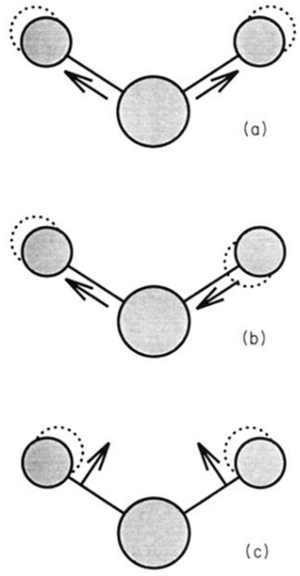

FIG. 2. The geometric content of the local modes: *A* depicts the symmetric stretching mode, *B* the antisymmetric stretching mode, and finally *C* the bending mode.