Comment on “Mean-field approach to the algebraic treatment of molecules: Bent molecules”

Serdar Kuyucak*

Department of Theoretical Physics, Research School of Physical Sciences, Australian National University,
Canberra, ACT 0200, Australia
(Received 1 March 1999)

Using analytical solutions of the mean fields, it is shown that the vibron model solution for water given by Shao et al. [Phys. Rev. A 47, 2064 (1993)] corresponds to a linear molecule. The numerical fit obtained in this paper appears to be a runaway solution, nothing to do with the actual properties of water molecule.

[S1050-2947(99)05412-8]

PACS number(s): 33.20.-t

The vibron model [1] is an algebraic approach to molecular spectroscopy, and as such, it does not have an immediate connection with the familiar geometric variables: bond lengths and angles. Such a connection can be established through mean-field theory (MFT) as demonstrated by Levia- tan and Kirson [2] and Shao et al. [3,4]. A common conclusion of these studies was that the vibron model Hamiltonians used in the analysis of bent molecules within the dynamical symmetry approach (e.g., [5]), in fact, corresponded to a linear molecule, and further it has nothing to do with the actual properties of water molecule.

The general two-body Hamiltonian considered by Shao et al. [4] for description of bent triatomic molecules has the form

\[ H = A_1C_2(O_1(4)) + A_2C_2(O_2(4)) + A_{12}C_2(O_{12}(4)) + \lambda (M_4 - M_3) + \mu M_3 + h_1 \hat{n}_{p_1}^2 + h_2 \hat{n}_{p_2}^2 + h_3 \hat{n}_{p_1} \hat{n}_{p_2} + B_1 \hat{L}_1 \cdot \hat{L}_1 + B_2 \hat{L}_2 \cdot \hat{L}_2 + B_3 \hat{L}_1 \cdot \hat{L}_2. \]

(1)

Here \( C_2(O(4)) = \hat{D} \cdot \hat{D} + \hat{L} \cdot \hat{L} \) is the Casimir operator of \( O(4) \). \( M_3 \) and \( M_4 \) are the Majorana operators of the combined groups \( U_{12}(3) \) and \( U_{12}(4) \), given by

\[ M_3 = 2 \left[ p_1^{\dagger} p_2^{\dagger} \right]^{(1)} \cdot \left[ \hat{p}_2 \hat{p}_1 \right]^{(1)}, \]

\[ M_4 = \left( s_1^{\dagger} p_2 - s_2^{\dagger} p_1 \right) \cdot \left( \hat{p}_2 s_1 - \hat{p}_1 s_2 \right) + M_3. \]

(2)

The dipole, angular momentum, and the \( p \)-boson number operators in Eq. (1) are defined, respectively, by

\[ \hat{D}_\mu = \left[ s^{\dagger} \hat{p} + \hat{p}^{\dagger} s \right]^{(\mu)}, \quad \hat{L}_\mu = -\sqrt{2} \left[ p^{\dagger} \hat{p} \right]^{(\mu)}, \]

\[ \hat{n}_p = \sum_\mu p_\mu p^{\dagger}_\mu. \]

(3)

where brackets denote tensor coupling and a tilde, \( \tilde{b}_{lm} = \left( -1 \right)^{l-m} b_{l-m} \). The \( n_p \) terms and \( M_4 \) in Eq. (1) belong to the \( u(3) \) algebras and are, thus, responsible for breaking of the \( O(4) \) dynamical symmetry. The energy surface of the Hamiltonian (1) is calculated using the condensate

\[ |N_1, N_2, r_1, r_2\rangle = (N_1! N_2!)^{-1/2} \left( b_1^{\dagger} \right)^{N_1} \left( b_2^{\dagger} \right)^{N_2} |0\rangle, \]

\[ b_1^{\dagger} = (1 + r_1^2)^{-1/2} \left( s_1^{\dagger} + r_1 p_1^{\dagger} \right), \]

\[ b_2^{\dagger} = (1 + r_2^2)^{-1/2} \left( s_2^{\dagger} + r_2 p_2^{\dagger} \right) + (\sin \theta) (p_2^{\dagger} - p_1^{\dagger} / \sqrt{2})], \]

(4)

where \( p_1 \) is aligned with the \( z \) axis and \( p_2 \) makes an angle \( \theta \) with it. Thus the bond angle is given by \( \theta_b = \pi - \theta \). In the special case of \( XY_2 \) molecules, appropriately to water, the energy surface is given by

\[ E(r, \theta) = \frac{N^2 r^2}{(1 + r^2)^2} \left[ 8 A + 4 A_{12} \cos \theta + (2 h + h_{12}) r^2 \right] + 2 \lambda (1 - \cos \theta) + \mu r^2 \sin^2 \theta. \]

(5)

Using the symmetry of \( XY_2 \) molecules, we have set here \( N_1 = N_2 = N \), \( r_1 = r_2 = r \), \( A_1 = A_2 = A \), and \( h_1 = h_2 = h \). Setting the derivatives of Eq. (5) with respect to \( r \) and \( \theta \) to zero, one obtains for the extremum conditions

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

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

(6)

TABLE I. Hamiltonian parameters (in cm\(^{-1}\)) used by Shao et al. [4] (top) and Iachello and Oss [5] (bottom) in fitting the spectrum of water. The rotational part of the spectrum was not studied in the latter, so \( B \) and \( B_{12} \) are not given.

<table>
<thead>
<tr>
<th>( A )</th>
<th>( A_{12} )</th>
<th>( \lambda )</th>
<th>( \mu )</th>
<th>( h )</th>
<th>( h_{12} )</th>
<th>( B )</th>
<th>( B_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>443.9</td>
<td>246.6</td>
<td>498.5</td>
<td>3,514</td>
<td>-532.3</td>
<td>988.1</td>
<td>392.1</td>
<td>-314.4</td>
</tr>
<tr>
<td>-15.826</td>
<td>-4.808</td>
<td>1.768</td>
<td>1.768</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
These equations can be solved analytically, yielding the following mean fields and the corresponding energies for the extremum points:

\[
\begin{align*}
\theta &= 0, \quad r^2_\theta = \frac{4A + 2A_{12}}{4A + 2A_{12} - 2h - h_{12}}, \\
E_0 &= -N^2 \frac{(4A + 2A_{12})^2}{-8A - 4A_{12} + 2h + h_{12}}, \\
E_\theta &= -N^2 \frac{(4A + 2A_{12})(4A - 2A_{12} + 2\lambda) - (2A_{12} - \lambda)^2(2h + h_{12})}{(2A_{12} - \lambda)^2 + (-8A - 2\lambda + 2h + h_{12})\mu}.
\end{align*}
\]

These solutions were not utilized by Shao et al. [4], who instead attempted a numerical fit of the ten model parameters (eight in the Hamiltonian and two in the dipole transition operator) to nine physical quantities of the water molecule constrained by the bond angle of \(\theta_b = 105^\circ\). The quantities used were the excitation energies and transition strengths of the three vibrational modes and the three components of the moment of inertia. The Hamiltonian parameters they obtained are listed in Table I. Substituting these values in Eq. (9) gives \(\cos \theta = -1.41\). That is, there is no bent minimum, and this Hamiltonian in fact describes a linear molecule with mean fields \(\theta = 0^\circ\) and \(r = 1.03\).

Shao et al. [4] compared their results with those of Ref. [5], where a fairly accurate description of the vibrational overtones in H\(_2\)O was given using the dynamical symmetry approach. However, they seem to have ignored the orders of magnitude difference between their parameters and those of Ref. [5] (see Table I). As a numerical diagonalization shows, these large parameter values lead to a similarly inflated spectrum compared to the actual one. The problem with the parameter set used in Ref. [4] may not be just one of scale, however. The amount of symmetry breaking invoked via the \(\hat{n}_p\) terms is also likely to cause problems. A recent study of the symmetry breaking in diatomic molecules shows that the \(O(4)\) symmetry is quite good, and only a small, perturbative breaking with the \(\hat{n}_p\) terms is required or allowed for realistic descriptions of molecular spectra [6,7]. A large symmetry breaking destroys the good agreement between experiment and theory at higher rotational and vibrational frequencies. Naturally such problems will not be apparent if one restricts the description of a spectrum to the first overtones, as has been done in Ref. [4]. However, one of the strong points of the vibron model is that it provides a simple framework for a complete description of molecular spectra including many overtones. Therefore, when alternative parametrizations are used, it would be essential to demonstrate that this feature of the model is maintained by going beyond the first overtones.

The analytic solutions for mean fields (7)–(9) enables one to study the shape-phase transitions in the vibron model without resorting to numerical methods. In this way, one can gain an intuitive understanding of the model space and the role each parameter plays in obtaining bent solutions. Such a study has recently been carried out [8], which reveals that Majorana interactions (and not the \(\hat{n}_p\) terms as claimed in Ref. [4]) play an essential role in driving a triatomic system from linear to a bent shape. Preliminary results indicate that the strength of the \(M_3\) term required to obtain a bent shape is beyond the perturbative range and, therefore, extensions of the model may be needed to describe the bent molecules. Details of a mean-field analysis of triatomic molecules in the vibron model, which utilizes the analytical solutions, is planned to be given in a forthcoming article.