Comment on “Boson-realization model for the vibrational spectra of tetrahedral molecules”

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An algebraic model in terms of a local harmonic boson realization was recently proposed to study molecular vibrational spectra [Zhong-Qi Ma et al., Phys. Rev. A 53, 2173 (1996)]. Because of the local nature of the bosons the model has to deal with spurious degrees of freedom. An approach to eliminate the latter from both the Hamiltonian and the basis was suggested. We show that this procedure does not remove all spurious components from the Hamiltonian and leads to a restricted set of interactions. We then propose a scheme in which the physical Hamiltonian can be systematically constructed up to any order without the need of imposing conditions on its matrix elements. In addition, we show that this scheme corresponds to the harmonic limit of a symmetry-adapted algebraic approach based on u(2) algebras. [S1050-2947(97)03811-0]

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I. INTRODUCTION

In a recent paper [1], Ma et al. proposed a model to describe the vibrational spectra of tetrahedral molecules and applied it to the methane molecule. The authors assign to each of the ten interatomic bonds a set of bosonic operators \( \{a_i^\dagger, a_i\} \), \( i = 1, 2, \ldots, 10 \), which satisfy the standard boson commutation relations

\[
[a_i, a_j^\dagger] = \delta_{i,j}, \quad [a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0.
\]

The first four operators \( i = 1, \ldots, 4 \) are chosen to correspond to the C-H bonds (stretching vibrations), while the last six \( i = 5, \ldots, 10 \) represent the H-H bonds (bending vibrations). The Hamiltonian is then expanded in terms of these operators. For methane they proposed the following \( T_d \)-invariant Hamiltonian:

\[
\hat{H} = \hat{H}_1 + \hat{H}_{2s} + \hat{H}_{2b},
\]

where \( \hat{H}_1 \) is a one-body contribution,

\[
\hat{H}_1 = \sum_{i=1}^{10} \sum_{j=1}^{4} a_i^\dagger a_i + \sum_{i=1}^{10} \sum_{j=1}^{4} \lambda_5 [ (a_5^\dagger a_5 + a_6^\dagger a_6 + a_{10}^\dagger a_{10}) + \text{H.c.} ] + \sum_{i=1}^{10} \sum_{j=5}^{10} \lambda_4 [ a_i^\dagger a_j + a_j^\dagger a_i + a_i a_j + a_j a_i ]
\]

and \( \hat{H}_{2s} \) corresponds to two-body anharmonic contributions to the stretching \((x=s)\) and bending \((x=b)\) vibrations,

\[
\hat{H}_{2s} = -X_s \sum_{i=1}^{4} \hat{N}_i (\hat{N}_i - 1) - X_s \sum_{i=1}^{4} a_i^\dagger a_i^\dagger a_i a_i,
\]

\[
\hat{H}_{2b} = -X_b \sum_{i=5}^{10} \hat{N}_i (\hat{N}_i - 1) - X_b \sum_{i=5}^{10} a_i^\dagger a_i^\dagger a_i a_i.
\]

In Eq. (3) we introduced \( \epsilon_s = \omega_s - 2X_s \) and \( \epsilon_b = \omega_b - 2X_b \). The number operator \( \hat{N}_i \) is defined as \( \hat{N}_i = a_i^\dagger a_i \). The Hamiltonian conserves the total number of quanta \( N = \sum_{i=1}^{10} \hat{N}_i \). Since the methane molecule has nine vibrational degrees of freedom, the operators \( \{a_i^\dagger, a_i\} \) give rise to ten degrees of freedom, spurious interactions may occur in \( \hat{H} \). Their identification, however, is not obvious when the Hamiltonian is written in the form of Eqs. (2)–(4). In [1] the authors proceed by identifying the spurious states as those containing the fully symmetric, one-quantum bending state \( \psi(A_1 \subset 100 \, 000) \) as a factor. With a combination of projection and coupling techniques and an orthogonalization procedure, the physical space up to three quanta is generated. Next it is shown that the physical Hamiltonian does not couple the physical states with the physical states as long as the conditions

\[
\lambda_5 = 0, \quad X_s = 0
\]

are imposed on the Hamiltonian of Eq. (2). Although these conditions indeed lead to the correct results, they are too restrictive and, furthermore, do not remove all spurious interactions.

II. SPURIOUS INTERACTIONS

In this section, we show that the condition of Eq. (5) is not sufficient to remove all spurious interactions from the Hamiltonian. We define a new set of harmonic bosons with well-defined tensorial properties under the tetrahedral \( T_d \)
group by projecting the local boson operators. For the stretching modes we have

$$s_{\Gamma,\gamma}^{\dagger} = \sum_{i=1}^{4} \alpha_{i}^{\Gamma,\gamma} a_{i}^{\dagger},$$

with $\Gamma = A_1, F_2$ and for the bending modes

$$b_{\Gamma,\gamma}^{\dagger} = \sum_{i=5}^{10} \beta_{i}^{\Gamma,\gamma} a_{i}^{\dagger},$$

with $\Gamma = A_1, E, F_2$, and similar expressions for the annihilation operators. The coefficients $\alpha_{i}^{\Gamma,\gamma}$ and $\beta_{i}^{\Gamma,\gamma}$ are the same as those appearing in the projected wave functions of Eqs. (3.1) and (3.2) in [1]. In the framework of this alternative scheme, both the Hamiltonian and the basis states are constructed by repeated coupling of these normal bosons. In this way, we obtain automatically an orthonormal symmetry-adapted basis with a well-defined number of quanta in each one of the fundamental vibrational modes. For example, with the usual notation for the normal modes of methane ($\nu_1, \nu_2, \nu_3, \nu_4$), we find for two quanta the following basis states with symmetry $A_1$:

$$|2,0,0,0\rangle = \frac{1}{\sqrt{2}} (s_{A_1}^{\dagger} s_{A_1}^{\dagger} A_{1}|0\rangle),$$

$$|0,2,0,0\rangle = \frac{1}{\sqrt{2}} (b_{E}^{\dagger} b_{E}^{\dagger} A_{1}|0\rangle),$$

$$|0,0,2,0\rangle = \frac{1}{\sqrt{2}} (s_{F_2}^{\dagger} s_{F_2}^{\dagger} A_{1}|0\rangle),$$

$$|0,0,0,2\rangle = \frac{1}{\sqrt{2}} (b_{F_2}^{\dagger} b_{F_2}^{\dagger} A_{1}|0\rangle),$$

$$|0,0,1,1\rangle = (s_{F_2}^{\dagger} b_{F_2}^{\dagger}) A_{1}|0\rangle).$$

Here $(\cdots)^{\Gamma}$ indicates coupling of two quanta to symmetry $\Gamma$. These basis states are orthogonal, since they correspond to eigenvectors associated with different eigenvalues of the number operators

$$\hat{n}_{\Gamma_1} = \sum_{\gamma} s_{\Gamma_1,\gamma}^{\dagger} s_{\Gamma_1,\gamma}, \quad \hat{n}_{\Gamma_2} = \sum_{\gamma} b_{\Gamma_2,\gamma}^{\dagger} b_{\Gamma_2,\gamma}.$$}

This symmetry-adapted procedure provides a method to remove the spurious interactions from the Hamiltonian as well as the spurious states from the basis. It consists in deleting the tensors which are associated with the spurious bending mode, $b_{A_1}^{\dagger}$ and $b_{A_1}$, in the construction of physical operators and basis states. This allows an exact elimination of the spurious states without the need to impose additional conditions on matrix elements.

The Hamiltonian of Eq. (2) does include spurious interactions. This can be seen by rewriting $\hat{H}$ in terms of the normal bosons of Eqs. (6) and (7). For the one-body Hamiltonian of Eq. (3) we find

$$\hat{H}_1 = (\epsilon_v + 3\lambda_1) \hat{n}_{A_1} + (\epsilon_v - \lambda_1) \hat{n}_{F_2} + (\epsilon_v + 5\lambda_2 + \lambda_3) \hat{n}_{A_1} +$$

$$+ (\epsilon_v - \lambda_2 + \lambda_3) \hat{n}_{F_2} + (\epsilon_v - \lambda_2 - \lambda_3) \hat{n}_{F_2} +$$

$$+ 2\sqrt{6}\lambda_4 [(s_{F_2}^{\dagger} b_{F_2}^{\dagger}) A_{1} + H.c.]$$

$$+ 2\sqrt{6}\lambda_5 [(s_{A_1}^{\dagger} b_{A_1}^{\dagger}) A_{1} + H.c.]$$

(10)

There are two terms that contain the spurious $A_1$ bending mode. This shows that, in order to remove the spurious interactions from $\hat{H}_1$, the condition $\lambda_2 = 0$ of Eq. (5) is not sufficient. In the present symmetry-adapted analysis we find two conditions: $\lambda_2 = 0$ and $\epsilon_v + 5\lambda_2 + \lambda_3 = 0$. We remark that, since the expectation value of $\hat{n}_{A_1}$ in the physical basis vanishes, the omission of the second condition has no further consequences.

A similar analysis can be carried out for the interactions in $\hat{H}_2$ and $\hat{H}_3$. The operators in Eq. (4) represent strong local interactions, and their representation in terms of the normal operators of Eqs. (6) and (7) acquires a complicated form which involves operators that transfer quanta between different modes. The Hamiltonian $\hat{H}_2$ only depends on the stretching modes and hence does not contain spurious interactions. However, the bending contribution $\hat{H}_3$ contains terms that transfer quanta between spurious and physical states. This can be seen by calculating its matrix elements in the basis states with $A_1$ symmetry that have two quanta in the bending vibrations

$$|\Gamma\rangle = \frac{1}{\sqrt{2}} (b_{E}^{\dagger} b_{E}^{\dagger}) A_{1}|0\rangle,$$

with $\Gamma = A_1, E$ and $F_2$, respectively. The states with $\Gamma = E, F_2$ belong to the physical basis of Eq. (8), whereas the state with $\Gamma = A_1$ is spurious. In this basis the matrix elements of $\hat{H}_3$ are

$$-X_b \begin{pmatrix} 1 & \sqrt{2} & 1 \\ 1 & 3 & 3 \\ \sqrt{2} & \frac{2}{3} & \sqrt{3} \end{pmatrix}.$$
In summary, in this section we have shown that in order to remove the spurious interactions from the Hamiltonian of [1] three conditions have to be fulfilled:

$$\lambda_5 = 0, \quad X_b = 0, \quad \epsilon_b + 5\lambda_2 + \lambda_3 = 0. \quad (13)$$

In the calculation of the vibrational spectrum of methane presented in [2], no stretching-bending interactions were included ($X_b = 0$). The spurious components in the Hamiltonian were removed by requiring that its expectation value in the spurious state with one quantum in the $A_1$ bending mode vanishes. This method leads to exact results in the harmonic limit as long as no higher-order interactions are considered, in which case it reduces to the last condition of Eq. (13).

An additional comment concerns the basis used in [1]. The basis functions in general do not carry the quantum numbers that correspond to the number of quanta in each of the normal vibrational modes. This represents a disadvantage in the process of identifying the calculated energies with the experimental ones, which are traditionally reported in terms of the maximum component in this basis. The same holds for the labeling of predicted states. This problem was overcome in [2] by constructing the physical basis by means of the $T_d$ Clebsch-Gordan coefficients. We note, however, that in Eq. (3.12) of [2] the normalization factor

$$\frac{1}{\sqrt{N_s N_b}} \sum_{\gamma} \hat{J}_{\mu, \gamma}^{\Gamma} \hat{J}_{\mu, \gamma}^{\Gamma}$$

was missing. When this factor is included, the coupling procedure is straightforward to apply and provides an orthonormal symmetry-adapted basis for the physical space with the desired labels ($\nu_1, \nu_2, \nu_3, \nu_4$).

### III. SYMMETRY-ADAPTED APPROACH

At this point we would like to mention that recently the U(2) model used in [2] has been further developed [3-6] by elaborating a tensorial formalism analogous to the one suggested above. In this symmetry-adapted approach the local $u_s(2)$ algebras \{\hat{G}_i\} = \{\hat{N}_i, \hat{J}_{+, \, i}, \hat{J}_{-, \, i}, \hat{J}_{0, \, i}\} are projected to $T_d$ tensors

$$\hat{T}^{\Gamma}_{\mu, \gamma} = \sum_{i=1}^{4} a_i^{\Gamma, \gamma} \hat{J}_{\mu, \gamma}^{i, \gamma}, \quad \hat{T}^{\Gamma}_{\mu, \gamma} = \sum_{i=5}^{10} b_i^{\Gamma, \gamma} \hat{J}_{\mu, \gamma}^{i, \gamma}, \quad \hat{T}^{\Gamma}_{\mu, \gamma} = \sum_{i=1}^{10} b_i^{\Gamma, \gamma} \hat{J}_{\mu, \gamma}^{i, \gamma}, \quad (15)$$

where $\mu = \pm$. The coefficients have the same meaning as in Eqs. (6) and (7). The $T_d$ invariant Hamiltonian is constructed by repeated couplings of these tensors to a total symmetry $A_1$. For example, the interactions that are at most quadratic in the generators and conserve the total number of quanta are given by

$$\hat{H}_{\Gamma} = \frac{1}{2 N_s^2} \sum_{\gamma} \left( \hat{T}^{\Gamma}_{+, \gamma} \hat{T}^{\Gamma}_{+, \gamma} + \hat{T}^{\Gamma}_{-, \gamma} \hat{T}^{\Gamma}_{-, \gamma} + \hat{T}^{\Gamma}_{0, \gamma} \hat{T}^{\Gamma}_{0, \gamma} \right),$$

$$\hat{H}_{\Gamma} = \frac{1}{2 N_s^2} \sum_{\gamma} \left( \hat{T}^{\Gamma}_{+, \gamma} \hat{T}^{\Gamma}_{+, \gamma} + \hat{T}^{\Gamma}_{-, \gamma} \hat{T}^{\Gamma}_{-, \gamma} + \hat{T}^{\Gamma}_{0, \gamma} \hat{T}^{\Gamma}_{0, \gamma} \right),$$

$$\hat{H}_{\Gamma} = \frac{1}{2 N_s^2} \sum_{\gamma} \left( \hat{T}^{\Gamma}_{+, \gamma} \hat{T}^{\Gamma}_{+, \gamma} + \hat{T}^{\Gamma}_{-, \gamma} \hat{T}^{\Gamma}_{-, \gamma} + \hat{T}^{\Gamma}_{0, \gamma} \hat{T}^{\Gamma}_{0, \gamma} \right). \quad (16)$$

Here $\Gamma = A_1, F_2$ for stretching vibrations ($x = s$) and $\Gamma = E, F_2$ for bending vibrations ($x = b$). The harmonic limit of these interactions is found by taking the limit $N_i \rightarrow \infty$, so that

$$\lim_{N_i \rightarrow \infty} \hat{J}_{\mu, \gamma}^{a_i} = a_i, \quad \lim_{N_i \rightarrow \infty} \hat{J}_{\mu, \gamma}^{a_i} = a_i, \quad \lim_{N_i \rightarrow \infty} \frac{2 \hat{J}_{\mu, \gamma}^{a_i}}{N_i} = 1, \quad \lim_{N_i \rightarrow \infty} \frac{\hat{J}_{\mu, \gamma}^{a_i}}{N_i} \rightarrow 0,$$

$$\lim_{N_s \rightarrow \infty} \frac{s_{\Gamma, \gamma}^{F_2, \gamma} + s_{\Gamma, \gamma}^{F_2, \gamma}}{N_s N_b} = 0, \quad \lim_{N_s \rightarrow \infty} \frac{b_{\Gamma, \gamma}^{F_2, \gamma} + b_{\Gamma, \gamma}^{F_2, \gamma}}{N_s N_b} = 0, \quad \lim_{N_s \rightarrow \infty} \frac{s_{\Gamma, \gamma}^{F_2, \gamma} + s_{\Gamma, \gamma}^{F_2, \gamma}}{N_s N_b} = 0,$$

where $a_i$ and $a_i^\dagger$ are the boson operators used in [1]. In this harmonic limit the interactions of Eq. (16) take the form

$$\lim_{N_s \rightarrow \infty} \frac{s_{\Gamma, \gamma}^{F_2, \gamma} + s_{\Gamma, \gamma}^{F_2, \gamma}}{N_s N_b} = 0, \quad \lim_{N_s \rightarrow \infty} \frac{b_{\Gamma, \gamma}^{F_2, \gamma} + b_{\Gamma, \gamma}^{F_2, \gamma}}{N_s N_b} = 0, \quad \lim_{N_s \rightarrow \infty} \frac{s_{\Gamma, \gamma}^{F_2, \gamma} + s_{\Gamma, \gamma}^{F_2, \gamma}}{N_s N_b} = 0,$$

which corresponds to the interactions appearing in Eq. (10), with the exception of the spurious interaction which, by construction, does not arise in this approach [6]. The symmetry-adapted basis states are constructed as in [2], but now taking into account the appropriate normalization coefficients of Eq. (14). The application of this model to the vibrational spectrum of methane yields a fit which is an order of magnitude more accurate than those of [1] and [2].

### IV. SUMMARY AND CONCLUSIONS

Summarizing, we have analyzed the boson-realization model presented by Ma et al. in [1] and found the following results.

(i) The approach presented in [1], although technically correct, does not remove all spurious interactions from the Hamiltonian. More significantly, the condition $X_b = 0$ elimi-
nates, in addition to spurious interactions, some physical interaction terms.

(ii) Although the method proposed to remove the spurious states gives the correct results, it becomes increasingly difficult to apply when additional higher-order interactions have to be included in the Hamiltonian.

(iii) In general, the basis in which the Hamiltonian is diagonalized does not carry the quantum numbers associated to the number of quanta in each fundamental vibrational mode. This problem can be solved either by using the $T_d$ Clebsch-Gordan coefficients or by diagonalizing the number operators of Eq. (9).

(iv) The formulation based on tensor operators provides a natural way to eliminate the spurious terms from the Hamiltonian and to construct higher-order interactions. Finally, we have shown that the approach of [1] corresponds to the harmonic limit of a more general method based on coupled U(2) algebras [3–6].

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