Are Linear Molecules Bent?!

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I. BACKGROUND

In the past several years, Hirano and coworkers published several papers[1–4] in which they advocated that linear molecules in their bending vibrational states look like "bent". More specifically the "expectation value" of the bending angle as defined in Fig.1 is not zero but takes some finite value. As one consequence, Nagashima et $al.$ argued that linear molecules were supposed to possess permanent dipole moments, and calculated the b-component of the permanent dipole moment of CO_2 [8].

The purpose of this presentation is to point out their confusing (erroneous) arguments. They utilized a modified theory originally developed by Hougen, Bunker, and Johns [5], and Bunker and Jensen [6, 7] for tri-atomic molecules (in particular for quasi-linear molecules). Their method treats molecular rotation and vibration simultaneously, and applied successfully for CH_2 and other quasi-linear molecules. Hougen, Bunker and Johns formulation was also applied to linear molecules.

II. LINEAR TRIATOMIC MOLECULE

Although the quantum mechanical theory on two-dimensional harmonic oscillators is well known, here we will summarize some important points to clarify the problematic discussions made by Hirano et $al.$ To compare the Hirano formulation later, we use the cylindrical coordinates for a degenerate isotropic harmonic oscillator,

$$q_a = Q \cos\phi \qquad (1)$$
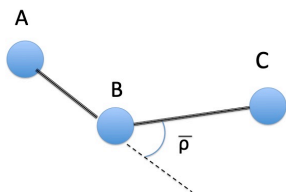$$q_b = Q \sin\phi, \qquad (2)$$

FIG. 1: Definition of the bending angle, $\bar{\rho}$.

where $Q = \sqrt{q_a^2 + q_b^2}$ and $\phi = \tan^{-1}(q_b/q_a)$. The ranges of the variables, Q and ϕ, are $0 \leq Q < \infty$ and $0 \leq \phi \leq 2\pi$.

In the cylindrical coordinates, the Hamiltonian is given with harmonic approximation as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{Q}\frac{\partial}{\partial Q}\left(Q\frac{\partial}{\partial Q}\right) - \frac{\hbar^2}{2\mu}\frac{1}{Q^2}\frac{\partial^2}{\partial \phi^2} + \frac{1}{2}kQ^2 \qquad (3)$$

The eigenfunction of the Schrödinger equation,

$$\hat{H}\Psi(Q,\phi) = E\Psi(Q,\phi) \qquad (4)$$

in terms of Q and ϕ are given by associated Laguerre polynomials and the usual angular part,

$$\Psi(Q,\phi) = N_{v\ell}e^{i\ell\phi}e^{-\frac{\alpha}{2}Q^2}Q^{|\ell|}L_{(v-|\ell|)/2}^{|\ell|}(\alpha Q^2) \qquad (5)$$

where $N_{v\ell}$ is the normalization constant, and $\alpha = \sqrt{\mu k/\hbar^2}$. The eigenvalue is given as

$$E = \hbar\omega(v+1) \qquad (6)$$

where $\omega = \sqrt{k/\mu}$ and $v - |\ell| = 0, 2, 4, \cdots$.

This function is of course equivalent to the linear combination of the products of the eigenfunctions for the harmonic oscillators in the Cartesian coordinate system.

III. FORMULATION BY HIRANO AND COWORKERS

Hirano et $al.$ claimed that the variable $\bar{\rho}$ and the angle χ, defined to be the rotation of the molecular plane relative to the "space fixed" coordinates, obey the same wave equation as eq. (3) with harmonic approximation with the potential energy defined as

$$U = \frac{1}{2}f\bar{\rho}^2. \qquad (7)$$

$$\hat{H}_H = -\frac{\hbar^2}{2\bar{\mu}}\frac{1}{\bar{\rho}}\frac{\partial}{\partial\bar{\rho}}\left(\bar{\rho}\frac{\partial}{\partial\bar{\rho}}\right) - \frac{\hbar^2}{2\bar{\mu}}\frac{1}{\bar{\rho}^2}\frac{\partial^2}{\partial\chi^2} + \frac{1}{2}f\bar{\rho}^2 \qquad (8)$$

See eq. (36) in Appendix of Ref. [3]. Note here that we have used a different notation $\bar{\mu}$ instead of μ used by Hirano et $al.$, because this quantity is the moment of inertia associated with $\bar{\rho}$, not the reduced mass. The Hamiltonians given as eq. (3) and as eq. (8) look exactly same. Then they claimed that the eigenfunction should be given the same function obtained by using the

standard cylindrical coordinate formalism, given in eq. (5),

$$\Psi_H(\bar{\rho}, \chi) = N'_{v\ell} e^{i\ell\chi} e^{-\frac{\alpha}{2}\bar{\rho}^2} \bar{\rho}^{|\ell|} L^{|\ell|}_{(v-|\ell|)/2}(\alpha\bar{\rho}^2), \quad (9)$$

where $0 \leq \bar{\rho} \leq \pi$ and $0 \leq \chi \leq 2\pi$. However, we should carefully examine if the function given as eq.(9) is really the eigenfunction for the Schrödinger equation given in eq. (8).

We really have to go back to elementary courses of quantum mechanics. The range of the variable $\bar{\rho}$ is $0 \leq \bar{\rho} \leq \pi$, as given in their papers. Remember that the eigenfunction given in terms of the Laguerre functions given as eq.(5) is obtained by imposing the boundary condition that the function should tend to zero as the variable $Q \to +\infty$. The range of $\bar{\rho}$ is restricted to $0 \leq \bar{\rho} \leq \pi$. As a quantum mechanical problem, consideration of the range of the variables and the boundary conditions are very important. Therefore the eigenfunction for the standard two-dimensional oscillator given in terms of the Laguerre polynomials cannot be the eigenfunction for the Hamiltonian used by Hirano $et\ al.$ Also the Hirano formulation cannot yield the eigenvalue for the bending vibration correctly. Hirano and coworkers wrote, "the wavefunction values are negligibly small for $Q > \eta$, and hence the size reduction in Q-interval makes no discernible difference."[2, 3] (Q and η are defined to be $Q = \sqrt{\mu}\bar{\rho}$ and $\eta = \sqrt{\mu}\pi$, respectively.) This statement indicates that they treat the quantum mechanical theory in quite casual fashion. Consequently we should cast doubt on their logic and their claim of "non-linearity of linear molecules".

Hirano $et\ al.$ made a statement that "Conventionally, the (Q, θ) expressions* are generally used by spectroscopists for a basic treatment of the doubly-degenerate bending motion since these expressions produce the justification for labeling the bending energy states by the quantum numbers v and ℓ."[3] This comment on spectroscopists and the quantum theory of doubly degenerate isotropic bending vibrations of linear molecules is hard to accept. Do they believe that their calculation that contradicts the well established quantum mechanical theory is correct? Do they assert that the standard quantum mechanical theory of bending vibrations is incorrect?

* Here the (Q, θ) expression means the formulation with the cylindrical coordinates $Q = \sqrt{q_a^2 + q_b^2}$ and $\theta = \tan^{-1}(q_b/q_a)$.

IV. CONCLUSION

Despite elaborate discussions made by Hirano $et\ al.$, their claim that linear molecules are (look) bend in the bending vibrational states (including the ground state?) sounds quite puzzling at best. If the potential energy for some molecules has minimum at the linear configuration, the molecules are linear.

We would like to encourage everyone to read, for example, Introduction of ref. [3]. We cite here only the last sentence of the Introduction, "We show that, in terms of averaged bending angle, any linear molecule in any vibrational state will necessarily be observed as being effectively bent. "Afterward, everyone would understand how different view on the molecular vibrations, in particular, on the bending vibrations of linear molecules they have, and their idea about the bending vibration seems to be worth more critical discussions, or simply ignore it.

Final comment. If we calculate the expectation value of $Q = \sqrt{q_a^2 + q_b^2}$, it yields positive value. The expectation value of the scalar positive physical quantity should be positive. However, it does not mean the molecule is bent. Never attempt to observe the b-component of the permanent dipole of CO_2. [8]

[1] T. Hirano, R. Okuda, U. Nagashima, and P. Jensen. $J.$ $Mol.$ $Spectrosc.$, **250**, 33–43 (2008).

[2] T. Hirano and U. Nagashima. $J.$ $Mol.$ $Spectrosc.$, **314**, 35–47 (2015).

[3] T. Hirano, U. Nagashima, and P. Jensen. $J.$ $Mol.$ $Spectrosc.$, **343**, 54–61 (2018).

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[5] J. T. Hougen, P. R. Bunker, and J. W. C. Johns. $J.$ $Mol.$ $Spectrosc.$, **34**, 136–172 (1970).

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[8] U. Nagashima, H. Li, P. Jensen, and T. Hirano. In $Paper$ $1E13,$ The $12th$ $Annual$ $Meeting$ of $Japan$ $Society$ for $Molecular$ $Science$ $(Fukuoka,$ $Japan),$ 2018.