Classical versus Quantum Structures: The Case of Pyramidal Molecules

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Summary. In a previous paper we proposed a model to describe a gas of pyramidal molecules interacting via dipole-dipole interactions. The interaction modifies the tunneling properties between the classical equilibrium configurations of the single molecule and, for sufficiently high pressure, the molecules become localized in these classical configurations. The model explains quantitatively the shift to zero-frequency of the inversion line observed upon increase of the pressure in a gas of ammonia or deuterated ammonia. Here we analyze further the model especially with respect to stability questions.

10.1 Introduction

The behavior of gases of pyramidal molecules, i.e., molecules of the kind XY_3 like ammonia NH_3, has been the object of investigations since the early developments of quantum mechanics [11]. In recent times the problem has been discussed again in several papers [4, 12, 17, 7, 13, 14] from a stationary point of view while in [8, 9, 10] a dynamical approach has been attempted. For a short historical sketch of the issues involved we refer to [4, 17, 13].

In [13] we have constructed a simplified mean-field model of a gas of pyramidal molecules which allows a direct comparison with experimental data. Our model predicts, for sufficiently high inter-molecular interactions, the presence of two degenerate ground states corresponding to the different localizations of the molecules. This transition to localized states gives a reasonable expla-

nation of the experimental results [1, 2, 3]. In particular, it describes quantitatively, without free parameters, the shift to zero-frequency of the inversion line of NH_3 and ND_3 on increasing the pressure.

In the present paper we first reconsider our model from the standpoint of stationary many-body theory, clarifying the meaning of the mean-field energy levels. We then analyze the mean field states with respect to the energetic stability. The conclusions agree with those found in [10] via a dynamical analysis of the same type of model to which dissipation is added.

10.2 The model

We model the gas as a set of two-level quantum systems, that mimic the inversion degree of freedom of an isolated molecule, mutually interacting via the dipole-dipole electric force.

The Hamiltonian for the single isolated molecule is assumed of the form $-\frac{\Delta E}{2}\sigma^x$, where σ^x is the Pauli matrix with symmetric and antisymmetric delocalized tunneling eigenstates φ_+ and φ_-,

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \varphi_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \varphi_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}. \qquad (10.1)$$

Since the rotational degrees of freedom of the single pyramidal molecule are faster than the inversion ones, on the time scales of the inversion dynamics set by ΔE the molecules feel an effective attraction arising from the angle averaging of the dipole-dipole interaction at the temperature of the experiment [15]. The localizing effect of the dipole-dipole interaction between two molecules i and j can be represented by an interaction term of the form $-g_{ij}\sigma_i^z\sigma_j^z$, with $g_{ij} > 0$, where σ^z is the Pauli matrix with left and right localized eigenstates φ_L and φ_R,

$$\sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \varphi_L = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \varphi_R = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \qquad (10.2)$$

The Hamiltonian for N interacting molecules then reads

$$H = -\frac{\Delta E}{2}\sum_{i=1}^{N} 1_1 \otimes 1_2 \otimes \cdots \otimes \sigma_i^x \otimes \cdots \otimes 1_N$$

$$-\sum_{i=1}^{N}\sum_{j=i+1}^{N} g_{ij}\, 1_1 \otimes \cdots \otimes \sigma_i^z \otimes \cdots \otimes \sigma_j^z \otimes \cdots \otimes 1_N. \qquad (10.3)$$

For a gas of moderate density, we approximate the behavior of the $N \gg 1$ molecules with the mean-field Hamiltonian

$$h[\psi] = -\frac{\Delta E}{2}\sigma^x - G\langle\psi, \sigma^z\psi\rangle\sigma^z, \qquad (10.4)$$

where ψ is the single-molecule state ($\langle \psi, \psi \rangle = 1$) to be determined self-consistently by solving the nonlinear eigenvalue problem associated to (10.4). The parameter G represents the dipole interaction energy of a single molecule with the rest of the gas. This must be identified with a sum over all possible molecular distances and all possible dipole orientations calculated with the Boltzmann factor at temperature T. Assuming that the equation of state for an ideal gas applies, we find [13]

$$G = \frac{4\pi}{9} \left(\frac{T_0}{T} \right)^2 P d^3, \tag{10.5}$$

where $T_0 = \mu^2 / (4\pi\varepsilon_0\varepsilon_r d^3 k_B)$, ε_0 and ε_r being the vacuum and relative dielectric constants, d the molecular collision diameter and μ the molecular electric dipole moment. Note that, at fixed temperature, the mean-field interaction constant G increases linearly with the gas pressure P.

10.3 Molecular states

The nonlinear eigenvalue problem associated to (10.4), namely

$$h[\psi_\mu]\psi_\mu = \mu\psi_\mu \qquad \langle \psi_\mu, \psi_\mu \rangle = 1, \tag{10.6}$$

has different solutions depending on the value of the ratio $G/\Delta E$. If $G/\Delta E < \frac{1}{2}$, we have only two solutions corresponding to the delocalized eigenstates of an isolated molecule

$$\psi_{\mu_1} = \varphi_+ \qquad\qquad \mu_1 = -\Delta E/2, \tag{10.7}$$
$$\psi_{\mu_2} = \varphi_- \qquad\qquad \mu_2 = +\Delta E/2. \tag{10.8}$$

If $G/\Delta E > \frac{1}{2}$, there appear also two new solutions,

$$\psi_{\mu_3} = \sqrt{\frac{1}{2} + \frac{\Delta E}{4G}}\, \varphi_+ + \sqrt{\frac{1}{2} - \frac{\Delta E}{4G}}\, \varphi_- \qquad \mu_3 = -G, \tag{10.9}$$

$$\psi_{\mu_4} = \sqrt{\frac{1}{2} + \frac{\Delta E}{4G}}\, \varphi_+ - \sqrt{\frac{1}{2} - \frac{\Delta E}{4G}}\, \varphi_- \qquad \mu_4 = -G, \tag{10.10}$$

which in the limit $G \gg \Delta E$ approach the localized states φ_L and φ_R, respectively. Solutions (10.9) and (10.10) are termed chiral in the sense that $\psi_{\mu_4} = \sigma^x \psi_{\mu_3}$.

The states ψ_μ determined above, are the stationary solutions $\psi(t) = \exp(i\mu t/\hbar)\psi_\mu$ of the time-dependent nonlinear Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(t) = h[\psi]\psi(t). \tag{10.11}$$

The generic state $\psi(t)$ solution of this equation has an associated conserved energy given by

$$\mathcal{E}[\psi] = -\frac{\Delta E}{2}\langle\psi, \sigma^x\psi\rangle - \frac{G}{2}\langle\psi, \sigma^z\psi\rangle^2. \tag{10.12}$$

The value of this functional calculated at the stationary solutions (10.7-10.10) provides the corresponding single-molecule energies $e_i = \mathcal{E}[\psi_{\mu_i}]$,

$$
\begin{aligned}
e_1 &= -\Delta E/2, \\
e_2 &= +\Delta E/2, \\
e_3 &= e_4 = -\frac{\Delta E}{2} - \frac{1}{2G}\left(\frac{\Delta E}{2} - G\right)^2.
\end{aligned}
\tag{10.13}
$$

These energies are plotted in Fig. 10.1 as a function of the ratio $G/\Delta E$. The state effectively assumed by the molecules in the gas will be that with the minimal energy, namely the symmetric delocalized state ψ_{μ_1} for $G/\Delta E < \frac{1}{2}$ or one of the two degenerate chiral states for $G/\Delta E > \frac{1}{2}$.
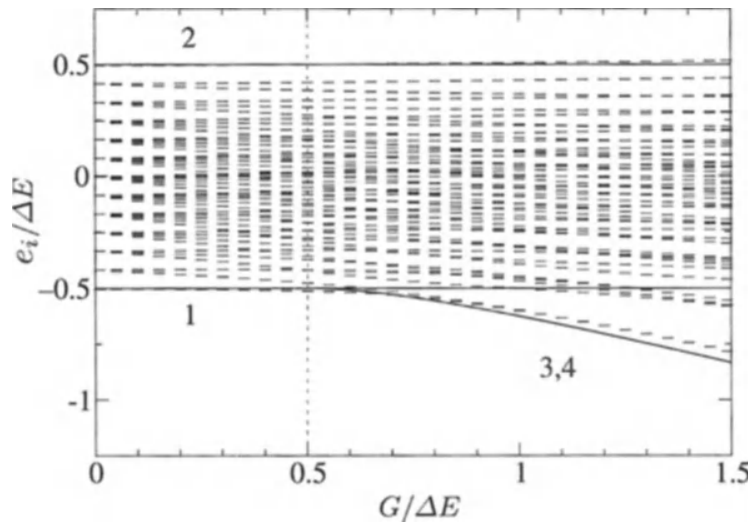

Fig. 10.1. Single-molecule energies e_i (solid lines) of the four stationary states ψ_{μ_i}, $i = 1, 2, 3, 4$, as a function of the ratio $G/\Delta E$. The dashed lines are the eigenvalues, divided by N, of the Hamiltonian (10.3) with $g_{ij} = G/N$ and $N = 12$.

The above results imply a bifurcation of the mean-field ground state at a critical interaction strength $G = \Delta E/2$. According to Eq. (10.5), this transition can be obtained for a given molecular species by increasing the gas pressure above the critical value

$$P_{\text{cr}} = \frac{9}{8\pi}P_0\left(\frac{T}{T_0}\right)^2, \tag{10.14}$$

where $P_0 = \Delta E/d^3$. In Table 10.1 we report the values of T_0 and P_0 calculated for different pyramidal molecules.

	ΔE (cm^{-1})	μ (Debye)	d (Å)	T_0 (Kelvin)	P_0 (atm)
NH_3	0.81	1.47	4.32	193.4	1.97
ND_3	0.053	1.47	4.32	193.4	0.13
PH_3	3.34×10^{-14}	0.57	–	29.1	8.11×10^{-14}
AsH_3	2.65×10^{-18}	0.22	–	4.3	6.44×10^{-18}

Table 10.1. Measured energy splitting ΔE, collision diameter d, and electric dipole moment μ, for different pyramidal molecules as taken from [16, 5]. In the fourth and fifth columns we report the temperature T_0 and the pressure P_0 evaluated as described in the text. In the case of PH_3 and AsH_3 the collision diameter, not available, is assumed equal to that measured for NH_3 and ND_3. We used $\varepsilon_r = 1$.

10.4 Inversion line

When a gas of pyramidal molecules which are in the delocalized ground state is exposed to an electromagnetic radiation of angular frequency $\omega_0 \sim \Delta E/\hbar$, some molecules can be excited from the state φ_+ to the state φ_-. For a non-interacting gas this would imply the presence in the absorption or emission spectrum of an inversion line of frequency $\bar{\nu} = \Delta E/h$. Due to the attractive dipole-dipole interaction, the value of $h\bar{\nu}$ evaluated as the energy gap between the many-body first excited level and the ground state is decreased with respect to the noninteracting case by an amount of the order of G. As shown in Fig. (10.2), the value of the inversion line frequency is actually a function of the number N of molecules and in the limit $N \gg 1$ approaches the mean field value [13]

$$\bar{\nu} = \frac{\Delta E}{h} \left(1 - \frac{2G}{\Delta E} \right)^{\frac{1}{2}}. \tag{10.15}$$

According to (10.15), the inversion line is obtained only in the range $0 \le G \le \Delta E/2$ and its frequency vanishes at $G = \Delta E/2$.

In [13] we have compared the mean field theoretical prediction for the inversion line with the spectroscopic data available for ammonia [1, 2] and deuterated ammonia [3]. In these experiments the absorption coefficient of a cell containing NH_3 or ND_3 gas at room temperature was measured at different pressures, i.e., according to (10.5) at different values of the interaction strength G. The measured frequency $\bar{\nu}$ decreases by increasing P and vanishes for pressures greater than a critical value. This behavior is very well accounted for by the the mean field prediction (10.15). In particular, the critical pressure evaluated according to Eq. (10.14) with no free parameters, at $T = 300$ K is $P_{\mathrm{cr}} = 1.695$ atm for NH_3 and $P_{\mathrm{cr}} = 0.111$ atm for ND_3 in very good agreement with the experimental data.
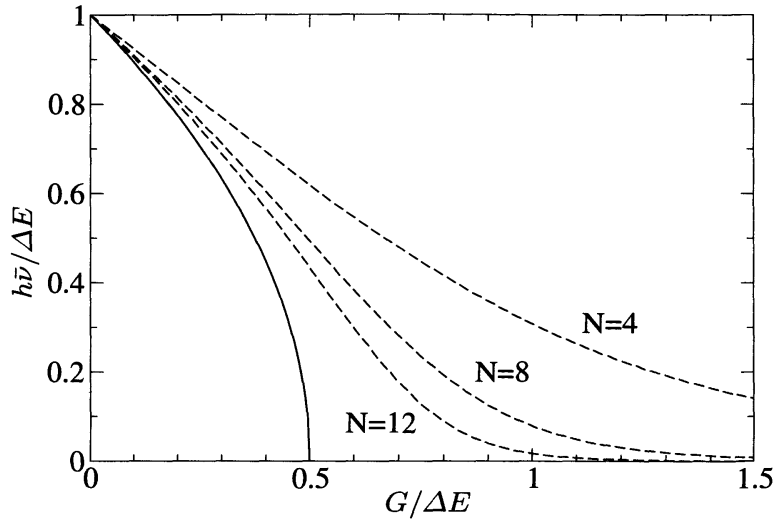
Fig. 10.2. Inversion line frequency as a function of the ratio $G/\Delta E$ in the mean field model (solid line) and obtained from the Hamiltonian (10.3) with $g_{ij} = G/N$ and $N = 4$, 8, and 12.

10.5 Energetic stability of the molecular states

In order to discuss the energetic stability of the mean field molecular states found in Section 10.3 we introduce the free energy $\mathcal{F}[\psi] = \mathcal{E}[\psi] - \mu\langle\psi,\psi\rangle$. The stationary solutions of Eq. (10.11) then can be viewed as the critical points of the Hamiltonian dynamical system

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi \\ \psi^*\end{pmatrix} = \begin{pmatrix}0 & 1 \\ -1 & 0\end{pmatrix}\begin{pmatrix}\frac{\delta\mathcal{F}[\psi]}{\delta\psi} \\ \frac{\delta\mathcal{F}[\psi]}{\delta\psi^*}\end{pmatrix}. \tag{10.16}$$

Under the effect of a perturbation which dissipates energy, a stationary state ψ_μ will remain stable only if $\mathcal{F}[\psi_\mu]$ is a minimum. Therefore we are interested in exploring the nature of the extremal values $\mathcal{F}[\psi_\mu]$ of the free energy functional. In general, this can be done in terms of the eigenvalues and the eigenvectors of the linearization matrix associated to the dynamical system (10.16) as explained in [6] for a Gross–Pitaevskii equation. Here, due to the simplicity of the model, we can provide a more direct analysis.

For a variation of the stationary solution $\psi_\mu \to \psi_\mu + \delta\phi$, up to the second order in $\delta\phi$, we have

$$\mathcal{F}[\psi_\mu + \delta\phi] = \mathcal{F}[\psi_\mu] + \delta^2\mathcal{F}[\psi_\mu, \delta\phi], \tag{10.17}$$

where

$$\delta^2\mathcal{F}[\psi_\mu, \delta\phi] = -\frac{\Delta E}{2}\langle\delta\phi, \sigma^x\delta\phi\rangle - \mu\langle\delta\phi, \delta\phi\rangle$$

$$-G\left(\langle\psi_\mu, \sigma^z\psi_\mu\rangle\langle\delta\phi, \sigma^z\delta\phi\rangle + \langle\psi_\mu, \sigma^z\delta\phi\rangle\langle\delta\phi, \sigma^z\psi_\mu\rangle\right.$$

$$\left.+\frac{1}{2}\langle\psi_\mu, \sigma^z\delta\phi\rangle^2 + \frac{1}{2}\langle\delta\phi, \sigma^z\psi_\mu\rangle^2\right). \tag{10.18}$$

The variation $\delta\phi$ can be taken in the most general form

$$\delta\phi = ae^{i\theta_a}\varphi_+ + be^{i\theta_b}\varphi_-, \tag{10.19}$$

where $\varphi_\pm$ are the delocalized tunneling eigenstates (10.1) and a, b, θ_a, and θ_b arbitrary real parameters with the constraint that $\langle\psi_\mu + \delta\phi, \psi_\mu + \delta\phi\rangle = 1 + \mathcal{O}(\delta\phi^2)$. By writing

$$\psi_\mu = a_\mu\varphi_+ + b_\mu\varphi_-, \tag{10.20}$$

with the real coefficients a_μ and b_μ deduced by Eqs. (10.7–10.10), the above constraint implies

$$a_\mu a \cos\theta_a + b_\mu b \cos\theta_b = 0. \tag{10.21}$$

The second variation of the free energy evaluated at the four stationary solutions ψ_{μ_i}, $i = 1, 2, 3, 4$, with the condition (10.21) gives

$$\delta^2\mathcal{F}[\psi_{\mu_1}] = G\ 2b^2\left(\frac{\Delta E}{2G} - \cos^2\theta_b\right), \tag{10.22}$$

$$\delta^2\mathcal{F}[\psi_{\mu_2}] = G\ 2a^2\left(-\frac{\Delta E}{2G} - \cos^2\theta_a\right), \tag{10.23}$$

$$\delta^2\mathcal{F}[\psi_{\mu_k}] = G\left[2a^2\left(1 + \frac{\Delta E}{2G}\right)\cos^2\theta_a + 2b^2\left(1 - \frac{\Delta E}{2G}\right)\cos^2\theta_b\right.$$
$$\left. + \left(a\sqrt{1 - \frac{\Delta E}{2G}}\sin\theta_a \mp b\sqrt{1 + \frac{\Delta E}{2G}}\sin\theta_b\right)^2\right], \tag{10.24}$$

where $k = 3, 4$ and the signs $\mp$ refer respectively to $k = 3$ and $k = 4$. We see that, for the state ψ_{μ_1}, the variation $\delta^2\mathcal{F}$ is always positive for $G < \frac{\Delta E}{2}$ and can be negative for $G > \frac{\Delta E}{2}$. The variation $\delta^2\mathcal{F}$ is always negative in the case of ψ_{μ_2}. For the states ψ_{μ_3} and ψ_{μ_4}, which exist only for $G > \frac{\Delta E}{2}$, the variation $\delta^2\mathcal{F}$ is always positive. We conclude that the free energy has a single minimum in correspondence of the delocalized state ψ_{μ_1} when $G < \frac{\Delta E}{2}$, and two degenerate minima in correspondence of the chiral states ψ_{μ_3} and ψ_{μ_4} when $G > \frac{\Delta E}{2}$. The energetic stability analysis is summarized in Table 10.2. Note that our results coincide with those reported in [10] where a standard linear stability analysis is performed for the same model considered here to which an explicit norm-conserving dissipation is added.

10.6 Conclusions

The specific prediction of our model for the critical pressure P_{cr} in terms of the electric dipole μ of the molecule, its size d, the splitting ΔE and the temperature T of the gas, successfully verified in the case of ammonia, could

	ψ_{μ_1}	ψ_{μ_2}	ψ_{μ_3}	ψ_{μ_4}
$\mathcal{F}[\psi_\mu]$	$-\Delta E$	$+\Delta E$	$\frac{G}{2}\left[1-\left(\frac{\Delta E}{2G}\right)^2\right]$	$\frac{G}{2}\left[1-\left(\frac{\Delta E}{2G}\right)^2\right]$
$G < \frac{\Delta E}{2}$	$\delta^2\mathcal{F} > 0$ minimum	$\delta^2\mathcal{F} < 0$ maximum		
$G > \frac{\Delta E}{2}$	$\delta^2\mathcal{F} \gtrless 0$ saddle point	$\delta^2\mathcal{F} < 0$ maximum	$\delta^2\mathcal{F} > 0$ minimum	$\delta^2\mathcal{F} > 0$ minimum

Table 10.2. Value of the free energy $\mathcal{F}[\psi_\mu]$ and sign of its second variation at the four extrema ψ_{μ_i}, $i = 1, 2, 3, 4$.

be experimentally tested also for other pyramidal gases for which Eqs. (10.14) and (10.15) predict the scaling law

$$\frac{\bar{\nu}_{XY_3}(P)}{\bar{\nu}_{XY_3}(0)} = \frac{\bar{\nu}_{X'Y_3'}(\gamma P)}{\bar{\nu}_{X'Y_3'}(0)}, \tag{10.25}$$

where $\gamma = P_{\mathrm{cr}\,X'Y_3'} / P_{\mathrm{cr}\,XY_3}$.

Our model applies not only to molecules XY_3 but also to their substituted derivatives $XYWZ$. An important difference between the two cases is that for XY_3 the localized states can be obtained one from the other either by rotation or by space inversion, while for $XYWZ$ they can be connected only by space inversion. This implies that $XYWZ$ molecules at a pressure greater than the critical value are chiral and therefore optically active. The measurement of the optical activity of pyramidal gases for $P > P_{\mathrm{cr}}$ would allow a direct verification of this prediction.

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