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# Critical conditions for a stable molecular structure

V Grecchi<sup>1</sup> and A Sacchetti<sup>2</sup>

<sup>1</sup> Dipartimento di Matematica, Università di Bologna, Piazza di Porta S Donato 5,  
I-40127 Bologna, Italy

<sup>2</sup> Dipartimento di Matematica, Università di Modena e Reggio Emilia, Via Campi 213/B,  
I-41100 Modena, Italy

E-mail: Grecchi@dm.unibo.it and Sacchetti@unimo.it

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## Abstract

Here, we show how the molecular structure appears and becomes stable for supercritical physical conditions. In particular we consider, for ammonia-type molecules, a simplified model based on a standard non-linear double-well Schrödinger equation with a dissipative term and a perturbative term representing weak collisions.

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## 1. Introduction

The empirical chemical models for molecules imply certain asymmetries and structures in apparent contradiction with quantum mechanical principles [1, 2].

The molecular structure is the result of a spontaneous symmetry breaking effect which would be explained by means of a quantum mechanical many body model, or better, a mean field one with non-linear terms. Thus, we have localized states of classical type. Such a strong and stable feature is expected to be the result of a critical phenomenon changing drastically the stationary quantum states.

As a particularly interesting example, we have pyramidal molecules such as the ammonia molecule  $\text{NH}_3$  (or  $\text{PH}_3$ ). To be clearer, following Wightman [3], it is better to consider the substituted molecule  $\text{NHDT}$  (or  $\text{PHDT}$ ), in which the three hydrogen nuclei are distinguished by isotopes. Such molecules should have a pyramidal structure with the HDT nuclei in a triangular basis and the nucleus N (or P) at a vertex, and a chirality, depending on the choice of the vertex. Quantum mechanics predicts symmetrical molecules with the nucleus N delocalized in both vertices. Indeed, in the Bohr–Oppenheimer approximation the nucleus N feels a double-well potential as was established by Hund in 1927 [4], and we have even and odd stationary states and beating bounded states. In fact, physically we do not observe the

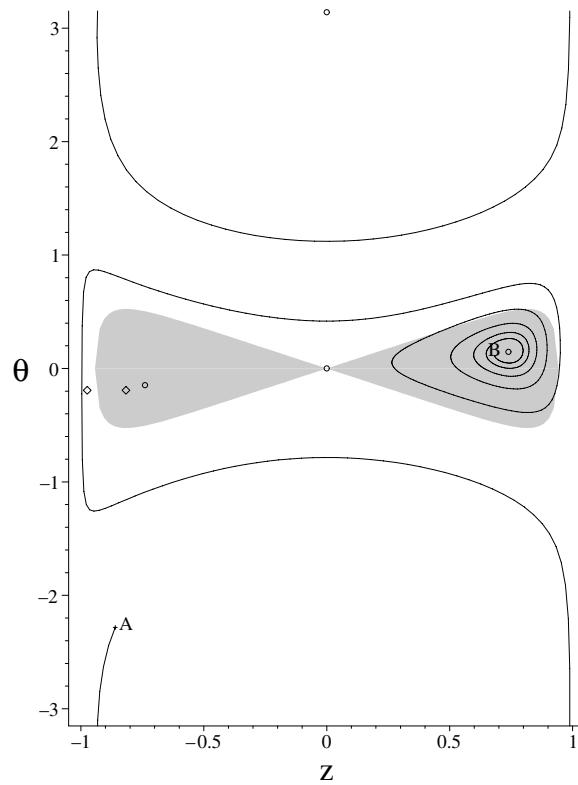
effect (an inversion line) of the beating in the case of  $\text{PH}_3$ . The cause of this phenomenon should be the polarity of the pyramidal molecule which polarizes the environment, so that the reaction field stabilizes the structure [5].

Following these ideas, Davies [6] and Pratt [7] suggested a non-linear Stark model successfully used in [8, 9], where it was proved that at the value  $\mu_c = 1$  of the dimensionless non-linearity parameter  $\mu$  there is the appearance of new asymmetric stationary states and for values of  $\mu$  larger than  $2\mu_c$  there is the destruction of the beating motion of the nucleus N. We underline that such a model is basically conservative, hence it is not able to definitely explain the relevant fact that an ammonia molecule goes towards a chiral configuration when the gas pressure is high enough. Meanwhile in [10] the same model has been studied in order to explain the spectral data of the inversion frequency obtaining that the non-linearity parameter  $\mu$  should be proportional to the pressure of the ammonia gas, that is  $1.7\mu$  corresponds to the physical value of the pressure (in atmospheres) at room temperature.

In this paper, we expand such a simplified basic model for the molecular structure by taking into account a *dissipative* term, which satisfies the conservation of the norm of the wavefunction. We do not discuss the detail of this term from a physical point of view, since the only relevant effect of this term is the *energy* loss, which is justified by electromagnetic radiation. As a result, the *energy* (2) relaxes towards local minima, and the amount of transferred energy dissipates into the environment (that is the other molecules of the gas), and it is not given back within any relevant period of time. As in the case of complex Ginzburg–Landau equations [11] and of Gross–Pitaevskii equations with weakly dissipative effects [12], we expect to observe vortex trajectories about the new asymmetric stationary solutions. As a result, the stability of chiral configurations for finite values of the non-linearity parameter follows. We emphasize that such a stability result would strengthen the results by [10] where, by means of perturbative techniques applied to states with energy close to local minima, they compute the frequency of the inversion motion of ammonia molecules for increasing gas pressure.

Furthermore, if we also take into account the effect of weak collisions then we find that a chiral configuration, which exists for a non-linearity parameter greater than  $\mu_c$ , is unstable if the non-linearity parameter is less than  $3\mu_c$ . Let us note that this stability result does not depend on the strength of the perturbation given by the weak collision. Introducing the collision term, we are taking into account the fluctuations absent in the mean field approximation. For larger values of this parameter, the chirality states become stable provided that the interval between two collisions is larger than the relaxation time, in order that, when a collision occurs, the state is near an asymmetric stationary state. This means that for a supercritical density of the molecules, we have a stable chirality for low enough temperature. In order to better understand the situation, consider figures 1 and 2 where the space of states is shown as a sphere projected on a square by a Mercator map. The two coordinates  $z$  and  $\theta$ , respectively, represent the imbalance variable (which measures the localization) and the relative phase of the components of the state with respect to the two localized states. A collision actually randomly changes  $\theta$  but not  $z$  (that is the typical decoherence mechanism). Thus, for  $\mu$  greater than  $3\mu_c$  (see figure 2), the line defined by a value of  $z$  equal to that of an asymmetric stationary state is fully contained in the *vibrational* region. In contrast, for  $\mu < 3\mu_c$  (see figure 1) we have that a change of  $\theta$ , due to a collision, could shift an asymmetric stationary state into the *beating* region.

In conclusion, here we propose a very basic model for the molecular structure which is based on a standard non-linear Schrödinger equation with double-well potential, and where chiral stable configurations are a result of dissipative terms.



**Figure 1.** In this figure we plot the parametric graph of the solution  $z(t), \theta(t)$  of equation (5) for a given initial condition (point A) in the case  $\mu = 1.5, \zeta = 0.2$ , point B denotes the position of the state at  $t = 10\tau$ . Circles denote the stationary solutions. In the non-dissipative case ( $\zeta = 0$ ) we have only *vibrational* motions around one well inside the grey region; outside the grey region, we have periodic *beating* motions between the two wells. Here,  $z$  denotes the imbalance function taking values in the interval  $[-1, +1]$  and  $\theta$  is an angle taking values in the interval  $(-\pi, +\pi)$ .

## 2. Description of the model

The Hamiltonian for a single ammonia molecule takes the form

$$H_0 = -\frac{\hbar^2}{2m} \Delta + V$$

where  $V$  is a double-well potential invariant under a coordinate reflection  $V = PVP$ , where  $P$  is the unitary symmetry operator representing the inversion of the  $n$ th coordinate

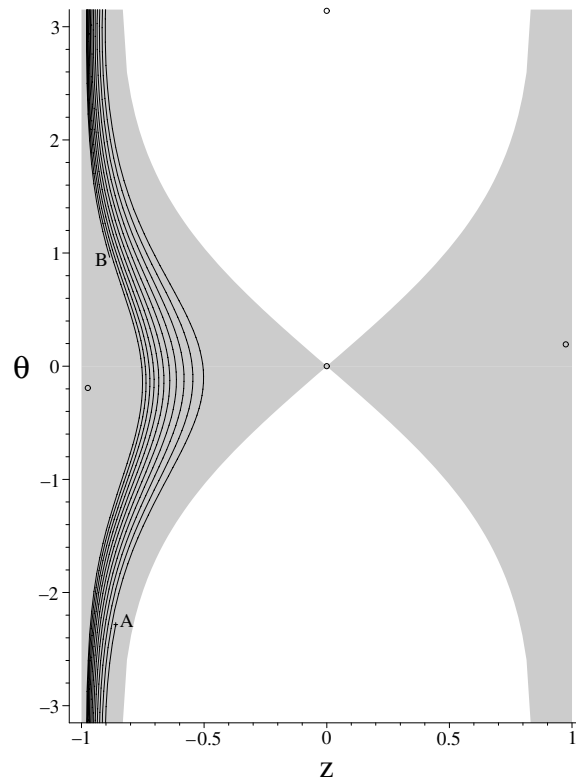
$$(x', x_n) \rightarrow (x', -x_n) \quad x' = (x_1, \dots, x_{n-1}) \quad n \geq 1.$$

The tunnelling time through the inter-well potential barrier is inversely proportional to the energy splitting  $\Delta E$  between the odd- and even-parity eigenstates  $|-\rangle$  and  $|+\rangle$  with energies  $\lambda_-$  and  $\lambda_+$ , and the solution of the unperturbed equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H_0 |\psi(t)\rangle$$

shows a beating motion between the two wells with period

$$\tau = \frac{2\pi\hbar}{\Delta E} \quad \Delta E = \lambda_- - \lambda_+.$$



**Figure 2.** In this figure we plot the parametric graph of the solution for a given initial condition (cross point) in the case  $\mu = 4.5$ ,  $\zeta = 0.2$ . Circles denote the stationary solutions.

The actual semi-classical parameter is the energy splitting  $\Delta E$ , and we choose the units such that  $\hbar = 1$ ,  $2m = 1$  and  $\Delta E \ll 1$ .

Let us consider the interaction of a single molecule with the other molecules of the gas. To this end, we take into account the attractive component of the intermolecular force between the ammonia molecules [13]. In the mean field approximation this term could be described by means of the effective potential depending on the wavefunction itself [10]:

$$W_{el} = W_{el}(|\psi\rangle) = \epsilon \nu g \quad \nu = \langle \psi | g | \psi \rangle \quad \epsilon < 0$$

where  $g$  is a bounded odd function,  $PgP = -g$ , and where  $\epsilon < 0$  measures the strength of the dipole–dipole interaction. The dynamics associated with the resulting Hamiltonian is such that we have conservation of the norm:

$$\langle \psi(t) | \psi(t) \rangle = \|\psi(t)\|^2 = 1 \quad (1)$$

and the conservation of the *energy* functional

$$\mathcal{E}(\psi) = \|\nabla \psi\|^2 + \langle \psi | V | \psi \rangle + \frac{1}{2} \epsilon \langle \psi | g | \psi \rangle^2. \quad (2)$$

Furthermore, if we regard the single ammonia molecule and the environment as the constituents of a conservative global system, then we also have to take into account a transfer of *energy* from the single ammonia molecule to the environment [14] due to the dipole radiation. Hence, we introduce a simple and basic *dissipative* term

$$W_{\text{dis}} = i\eta \nu g P \quad \eta < 0$$

satisfying the following physical prescriptions: a regular decrease of the *energy* (2), the preservation of the norm (1) and the dependence of this term on the mean value of the ammonia dipole;  $\eta$  measures the strength of the *dissipative* interaction. We do not try to relate this parameter to physical parameters until experimental data on substituted ammonia chirality appear. In such a way, the new effective Hamiltonian takes the form

$$H = H_0 + W \quad W = W_{el} + W_{dis}$$

where the term  $W$  is such that  $[TP, W] = 0$ , where  $T|\psi(t)\rangle = |\psi(t)\rangle^*$  is the time-reversal operator.

### 3. Main results

Here, we make use of the two-level model where we approximate the wavefunction  $|\psi(t)\rangle$  by means of its projection on the two lowest states. In particular, in such an approximation the total wavefunction of the system may be expanded as

$$|\psi(t)\rangle = a_R(t)|R\rangle + a_L(t)|L\rangle \quad (3)$$

where

$$|R\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle) \quad |L\rangle = \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle)$$

are the right- and left-hand states; they are such that  $P|R\rangle = |L\rangle$ . The normalization condition (1) on the wavefunction  $|\psi(t)\rangle$  implies that  $|a_R|^2 + |a_L|^2 = 1$ .

By substituting  $|\psi(t)\rangle$  by (3) in the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle$$

it follows that the expansion coefficients  $a_R$  and  $a_L$  have to satisfy the following system of ordinary differential equations:

$$\begin{cases} i\dot{a}_R = \Omega a_R - \omega a_L + \epsilon v c a_R + i\eta v c a_L \\ i\dot{a}_L = \Omega a_L - \omega a_R - \epsilon v c a_L - i\eta v c a_R \\ v = c(|a_R|^2 - |a_L|^2) \end{cases} \quad (4)$$

where

$$\omega = \frac{1}{2}(\lambda_- - \lambda_+) \quad \Omega = \frac{1}{2}(\lambda_- + \lambda_+)$$

and where we set

$$c = \langle R|g|R\rangle = -\langle L|g|L\rangle.$$

In order to study the beating motion, it is convenient to introduce the relative phase

$$\theta = \arg(a_R) - \arg(a_L)$$

which is a torus variable, and the imbalance variable

$$z = |a_R|^2 - |a_L|^2$$

which takes values in the interval  $[-1, +1]$ . They have to satisfy the system of ordinary differential equations

$$\begin{cases} \dot{z} = \omega Z(z, \theta) \\ \dot{\theta} = \omega \Theta(z, \theta) \end{cases} \quad (5)$$

where

$$Z(z, \theta) = 2\sqrt{1 - z^2} [\sin \theta - \zeta z \cos \theta]$$

and

$$\Theta(z, \theta) = -2 \frac{z}{\sqrt{1-z^2}} [\cos \theta + \zeta z \sin \theta] + 2\mu z$$

and

$$\mu = -c^2 \epsilon / \omega \quad \zeta = -c^2 \eta / \omega.$$

Here,  $\mu$  and  $\zeta$  represent positive dimensionless parameters that measure the effective non-linearity and the dissipation, respectively.

We observe the existence of the critical value  $\mu_c = 1$  for the non-linearity parameter  $\mu$ . We consider, first, the *weak non-linearity* case such that  $\mu < \mu_c$ . In such a case, equation (5) admits just two stationary solutions corresponding to the unperturbed even- and odd-parity eigenstates:  $z_1 = 0$  and  $\theta_1 = 0$ , corresponding to the even-parity eigenstate, is a *stable* stationary solution, and  $z_2 = 0$  and  $\theta_2 = \pi$ , corresponding to the odd-parity eigenstate, is an *unstable* stationary solution.

Then, we consider the *strong non-linearity* case such that  $\mu > \mu_c$ . The value  $\mu_c$  is a bifurcation point for the stable stationary solution [8] and for  $\mu > \mu_c$  we have four stationary solutions; two of them still correspond to the unperturbed even- and odd-parity eigenstates, the other two correspond to asymmetric states that, in the limit of large non-linearity, are fully localized on just one of the two wells. The stationary solution  $z_1 = 0$  and  $\theta_1 = 0$ , corresponding to the even-parity eigenstate, is a *saddle point* for  $\mu > \mu_c$ ; the stationary solution  $z_2 = 0$  and  $\theta_2 = \pi$ , corresponding to the odd-parity eigenstate, is still an *unstable* solution;  $z_3 = \sqrt{(\mu^2 - 1)/(\mu^2 + \zeta^2)}$  and  $\theta_3 = \arctan(\zeta z_3)$ , and  $z_4 = -z_3$  and  $\theta_4 = -\theta_3$  are *stable* asymmetric stationary solutions. Thus, any state generically goes near to one of these two asymmetric stationary states.

Therefore, in the strong non-linearity case we have that any initial state, except the two even- and odd-parity unperturbed eigenstates, finally goes to one of the two asymmetric stationary eigenstates giving a chiral configuration for the substituted ammonia molecule.

Now, we show that this chiral configuration is stable with respect to collisions when the density is large enough, and the temperature is low enough. We assume that the thermal energy at room temperature is smaller than the distance between the doublet  $\{\lambda_{\pm}\}$  and the other energy levels, so that the validity of the two-level approximation holds, and it is much larger than the splitting energy, so that a collision could produce a strong variation of the *energy*  $\mathcal{E}(\psi)$ .

To this end, we introduce a simplified model for molecular collision. When the single molecule undergoes a collision we add to the Hamiltonian  $H$  a perturbative term of the type  $f(x)v(t)$  where  $f(x)$  is a function with compact support and  $v(t)$  is a given time-dependent function. For instance, let  $v(t) = \chi_{t_1, t_2}(t)$  where  $\chi$  is the characteristic function on the interval  $[t_1, t_2]$ , and where we assume that the perturbation acts for a time much shorter than the beating period, that is

$$t_2 - t_1 \ll \tau. \quad (6)$$

Equation (4) then takes the form

$$\begin{cases} \dot{a}_R = \Omega a_R - \omega a_L + \epsilon v c a_R + i \eta v c a_L + v(t) c_R a_R \\ \dot{a}_L = \Omega a_L - \omega a_R - \epsilon v c a_L - i \eta v c a_R + v(t) c_L a_L \\ c_R = \langle R | f | R \rangle \quad c_L = \langle L | f | L \rangle \end{cases}$$

since

$$\langle R | f | L \rangle = \overline{\langle L | f | R \rangle} \sim 0.$$

Hence, the system (5) takes the form

$$\begin{cases} \dot{z} = \omega Z(z, \theta) \\ \dot{\theta} = \omega \Theta(z, \theta) + (c_R - c_L) v(t) \end{cases}$$

from which it follows that  $|z(t_2) - z(t_1)| \ll 1$ , since (6), and where it is not possible to obtain a similar bound for  $\theta$  when  $c_R \neq c_L$ .

This fact, that is the relative phase is strongly modified after a generic collision (such that  $c_R \neq c_L$ ), does not actually destroy the chiral configuration of a localized ammonia molecule if the pressure is high enough, i.e. such that  $\mu > 3\mu_c$ . Indeed, in such a case we have that the stable solution  $(z_3, \theta_3)$  (respectively  $(z_4, \theta_4)$ ) has a basin of attraction containing the strip  $z \geq z^*$  (respectively  $z \leq -z^*$ ) if  $\zeta$  is small enough and where  $z^* = 2\sqrt{2}/3 < z_3$ . We explain this fact by means of a continuity argument in the limit of  $\zeta = 0$ . Indeed, in such a limit we have the existence of two separatrix lines [9, 15] starting from the stationary solution  $(z_1, \theta_1)$  and satisfying the equation

$$\sqrt{1 - z^2} \cos \theta + \frac{1}{2}\mu z^2 = 1.$$

It is not difficult to see (2) that these paths are contained in the strip  $-z^* \leq z \leq z^*$  if  $\mu > 3\mu_c$ . As a result, it follows that a perturbation due to a collision acting in an interval of the order (6) shifts a state initially near to one of the asymmetric stationary stable eigenstates, to a state belonging to the basin of attraction of the stationary eigenstate itself. In particular, the state will always be far enough from the unstable stationary state and thus, after a finite time depending on  $\zeta$ , it returns near to the initial stationary state without visiting the other well, provided that in this period another collision does not occur. This condition should be fulfilled if the temperature is low enough.

Finally, let us note that the molecular structure is not completely stable for strong collisions (indeed, we have the phenomenon of racemization which makes the statistical mean of the chirality vanish at large time) and that an external electromagnetic field in the radio frequency range could destroy the molecular structure.

#### 4. Conclusion

In conclusion, we have shown that a simple dissipative non-linear model is able to explain the molecular structure of symmetrical molecules. Such chiral configurations are stable for weak collisions provided that the non-linearity parameter is larger than the critical value  $3\mu_c$ , and that the frequency collisions are small enough with respect to the rate of the energy decrease. This model would represent a significant improvement with respect to the previous simpler ones [16] where the effect of the environment was described by means of an external periodic perturbation superimposed onto a linear double-well Hamiltonian. In that case the relevance of the metastability on the localization was exploited. The kind of trap we propose here is simple, but not trivial, and in any case is able to make the spontaneous symmetry breaking given by the non-linearity stable. It could be relevant in the theory of decoherence, related to the appearance of classical mechanics, and in the study of many irreversible processes. As clearly appears in this paper, we have only considered the spontaneous symmetry breaking effect. In fact, one enantiomer may become dominant. This effect could be explained by means of the parity violation for weak nuclear interactions [17], largely amplified during the dynamics of the system [18, 19].

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