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Stationary states of pyramidal molecules coupled to an electromagnetic field below and above critical pressure

Vikram Athalye¹ and Arvind Kumar²

¹ Department of Physics, Thakur College, University of Mumbai, Mumbai 400 101, India

² HBCSE, Tata Institute of Fundamental Research, Mumbai 400 088, India

E-mail: vikathalye@yahoo.com and arvindk@hbcse.tifr.res.in

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Abstract

In this paper, we extend the analysis of stationary states of a nonlinear model of a gas of pyramidal molecules (already discussed in the literature) by including a linear coupling to an external electromagnetic field. It is seen that this results in a shift of the bifurcation point and consequently allows, for appropriate values of Rabi frequency, stable localized stationary solutions below the critical pressure required in the absence of molecule–field coupling.

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1. Introduction

In 1927, Hund anticipated the (now well known) problem of optical enantiomers [1], namely their nonexistence in energy eigenstates that are the superposition of the two enantiomeric (*left*-handed and *right*-handed) forms. These so-called *chiral* states, for example, of the molecules of the type XYZW, are mirror images of each other. Hund suggested a double-well potential model for the nucleus of X to describe its beating motion across the plane formed by the other three atoms. The *left*- and *right*-handed states ($|L\rangle$ and $|R\rangle$) then can be viewed as the states *localized* in the two minima of such a potential. The tunnelling from $|L\rangle$ to $|R\rangle$ and $|R\rangle$ to $|L\rangle$ leads to the so-called *inversion spectrum* from such molecules.

In late 1940s and early 1950s, there were a few spectroscopic investigations regarding such spectra from pyramidal molecules [2–4]. It was found that the frequency of the inversion line, which corresponds to the energy difference between the two lowest lying energy eigenstates, decreases to zero at a critical value of pressure, which is different for different pyramidal molecules. This ultimately leads to the disappearance of the inversion spectrum from the molecule and appearance of *chiral* or *localized* states of such molecules, which are found to be stable above the critical pressure.

In the last few years, there have been various theoretical proposals to explain this kind of transition to the optical enantiomeric states [5–13]. In the proposal of Jona-Lasinio,

Presilla and Toninelli [9], a nonlinear two-level model of a gas of pyramidal molecules was successfully employed to explain quantitatively, without free parameters, the shift to zero frequency of the inversion line. The nonlinearity in this model arises from the intermolecular dipolar interaction expressed in the mean-field approximation. In [10], they analysed the model further with respect to the energetic stability of the molecular states.

More recently, Grecchi and Sacchetti [13] considered a dissipative interaction of the molecule with its environment and showed that the stable chiral states are the result of the dissipative interaction. In this proposal, the nonlinear differential equations, representing the time derivatives of the imbalance variable z and the relative phase θ (see below), contained two parameters: μ the nonlinearity parameter and ζ , the dissipation parameter respectively. μ was related linearly to the pressure [9] while ζ was not related to any experimentally observable physical parameter. There exists a value of μ , namely $\mu_c = 1$, corresponding to the critical value of pressure, at which the bifurcation takes place giving rise to asymmetric localized stable stationary solutions apart from the already existing even and odd parity stationary solutions, for $\mu > \mu_c$.

In the present paper, we apply this analysis to a pyramidal molecule coupled to an external electromagnetic field through a linear interaction and analyse among other things, the shift in the bifurcation point due to molecule–field coupling. The paper is organized as follows: in section 2, the generalized Hamiltonian, which includes the Jaynes–Cummings Hamiltonian term in the rotating wave approximation representing the molecule–field interaction, is introduced. In section 3, using the total Hamiltonian we derive the system of generalized nonlinear differential equations representing the time derivatives of the imbalance variable z and the relative phase θ [13]. Apart from the effective nonlinearity and dissipation parameters of the earlier analysis, there appears a new parameter μ_0 in our case, representing the ratio of quantum Rabi frequency and the frequency corresponding to the energy difference between the two lowest lying energy states of the molecule. Further in the section, we obtain a polynomial of degree 4 in z and a relation expressing θ in terms of z , as the simultaneous conditions on (z, θ) to be a stationary solution. Both these expressions reduce to the results found in the earlier analysis in the absence of molecule–field coupling. Numerical solution of the polynomial equation in z shows a shift in the bifurcation point from the value $\mu_c = 1$ to a value depending on the Rabi frequency and the detuning and dissipative parameters. We conclude by giving examples of the required values of Rabi frequency for given values of α, ζ, μ and for chosen values of z_0 .

2. The model and the Hamiltonian

The Hamiltonian for a single pyramidal molecule has the form

$$H_M = -\frac{\hbar^2}{2m}\Delta + V \quad (1)$$

where V takes the form of a double-well potential. The stationary solutions of the equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H_M |\psi(t)\rangle \quad (2)$$

are the even- and odd-parity eigenstates $|1\rangle$ and $|2\rangle$ with energy eigenvalues E_1 and E_2 respectively. The time interval τ given by $\tau = \frac{2\pi\hbar}{\Delta E}$ with $\Delta E = E_2 - E_1$ is the period and $2\omega = \frac{\Delta E}{\hbar}$ is the frequency of the beating motion between the two wells.

For a molecule coupled to electromagnetic field and interacting with other molecules in the surroundings through the dipole–dipole and dissipative interactions [13], the total Hamiltonian is given by

$$H_{\text{total}} = H_M \otimes I_F + I_M \otimes H_F + H_{\text{MM}} \otimes H_f + H_{\text{Dis}} \otimes H_f + H_{\text{MF}}. \quad (3)$$

Here H_M is as given by (1); $H_F = \hbar\omega_0 a^\dagger a$ is the field Hamiltonian with a and a^\dagger being mode operators for the single-mode field; I_M and I_F are the identity operators acting on the molecular and field states respectively; $H_{\text{MM}} = \varepsilon\nu G$ (where, in terms of the total wavefunction, ν is defined by $\nu = \langle \Psi | G \otimes H_f | \Psi \rangle$) represents the molecule–molecule dipolar interaction in the mean-field approximation; G is a bounded odd function and $\varepsilon < 0$ measures the strength of the interaction; $H_{\text{Dis}} = i\eta\nu GP$ is the dissipative-interaction term; $\eta < 0$ measures the strength of the dissipative interaction; $H_{\text{MF}} = \hbar g(a^\dagger|1\rangle\langle 2| + a|2\rangle\langle 1|)$ is the Jaynes–Cummings Hamiltonian representing the molecule–field interaction and g is an effective coupling constant; $H_f = \frac{a+a^\dagger}{\sqrt{n+1}}$, an operator operating on the field kets, is introduced in the model to consider the concomitant creation and destruction of field quanta in the dipolar as well as dissipative interactions of the molecule with its surroundings.

3. Generalized nonlinear differential equations and their stationary solutions

The total (molecule–field) wavefunction at any time is given by

$$|\Psi(t)\rangle = a_1(t)|1\rangle|n+1\rangle + a_2(t)|2\rangle|n\rangle \quad (4)$$

where $|1\rangle = \frac{1}{\sqrt{2}}[|R\rangle + |L\rangle]$ and $|2\rangle = \frac{1}{\sqrt{2}}[|R\rangle - |L\rangle]$ as expressed in terms of the right- and left-handed states; $|n\rangle$ and $|n+1\rangle$ are the usual photon number states. Substitution of (4) in the time-dependent Schrödinger equation $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H_{\text{total}} |\Psi(t)\rangle$ gives

$$i\hbar \dot{a}_1 = a_1(t)[E_1 + \hbar\omega_0(n+1)] + a_2(t)[\hbar g\sqrt{n+1} + \varepsilon\nu c + i\eta\nu c] \quad (5a)$$

$$i\hbar \dot{a}_2 = a_1(t)[\hbar g\sqrt{n+1} + \varepsilon\nu c + i\eta\nu c] + a_2(t)[E_2 + \hbar\omega_0 n]. \quad (5b)$$

Using the relations $a_1(t) = \frac{a_R(t)+a_L(t)}{\sqrt{2}}$ and $a_2(t) = \frac{a_R(t)-a_L(t)}{\sqrt{2}}$, one can obtain the following system of ordinary differential equations,

$$i\dot{a}_R = \Omega a_R - \frac{\delta}{2} a_L + \varepsilon\nu c a_R - i\eta\nu c a_L + g\sqrt{n+1} a_R + \omega_0 \left(n + \frac{1}{2}\right) a_R \quad (6a)$$

$$i\dot{a}_L = \Omega a_L - \frac{\delta}{2} a_R - \varepsilon\nu c a_L - i\eta\nu c a_R - g\sqrt{n+1} a_L + \omega_0 \left(n + \frac{1}{2}\right) a_L \quad (6b)$$

$$\dot{\nu} = c[|a_R|^2 - |a_L|^2] \quad (6c)$$

where $\Omega = \frac{E_1+E_2}{2\hbar}$, $\omega = \frac{E_2-E_1}{2\hbar}$, $\delta = 2\omega - \omega_0$ and $c = \langle R|G|R\rangle = -\langle L|G|L\rangle$. Using equations (6), we find that the time derivatives of the relative phase variable $\theta = \arg(a_R) - \arg(a_L)$ and the imbalance variable $z = |a_R|^2 - |a_L|^2 \in [-1, +1]$ take the following generalized forms,

$$\dot{z} = \omega Z(z, \theta) \quad (8a)$$

$$\dot{\theta} = \omega \Theta(z, \theta) \quad (8b)$$

where

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

and

$$\Theta(z, \theta) = -2 \frac{z}{\sqrt{1-z^2}} [\alpha \cos \theta + \zeta z \sin \theta] + 2\mu z + 2\mu_0,$$

with

$$\alpha = \left(1 - \frac{\omega_0}{2\omega}\right), \quad \mu = \frac{-c^2 \varepsilon}{\omega}, \quad \zeta = \frac{-c^2 \eta}{\omega}, \quad \text{and} \quad \mu_0 = \frac{-g\sqrt{n+1}}{\omega}.$$

Here, μ and ζ , as earlier, represent positive dimensionless parameters that measure the effective nonlinearity and the dissipation, respectively; μ_0 is also a dimensionless parameter representing the ratio of the Rabi frequency of the driving field ' $-2g\sqrt{n+1}$ ' and the frequency ' 2ω ' corresponding to the energy difference between the two lowest lying energy levels of the molecule.

The stationary solutions (z_0, θ_0) , for which $\dot{z} = f_1(z, \theta)$ and $\dot{\theta} = f_2(z, \theta)$ are simultaneously equal to zero, are given by

$$(\zeta^2 + \mu^2)z_0^4 + (\mu_0^2 + \alpha^2 - \mu^2)z_0^2 + 2\mu\mu_0(z_0^3 - z_0) = \mu_0^2 \quad (9a)$$

$$\theta_0 = \tan^{-1} \left(\frac{\zeta z_0}{\alpha} \right). \quad (9b)$$

From (9a) μ_0 is given by

$$\mu_0 = z_0 \left[\sqrt{\frac{\alpha^2 + \zeta^2 z_0^2}{1 - z_0^2}} - \mu \right]. \quad (10)$$

(Only the positive square root in the bracket gives the correct limiting situation of $\mu_0 = 0$, $z_0 \neq 0$ since $\mu > 0$; so the negative root has been suppressed.)

Equations (9) and (10) are the main result of this paper. At a given pressure, i.e. for a fixed μ , equation (10) determines μ_0 for a specific value of z_0 , i.e. it tells us the value of Rabi frequency for a required value of the localization parameter. Let us consider the following cases:

Case (i). $\mu = \zeta = 0 \Rightarrow z_0^2 = \frac{\mu_0^2}{\mu_0^2 + \alpha^2}$: this is a well-known quantum optical result for the Jaynes–Cummings model in which the molecule possesses 'dressed' states corresponding to the combinations of its two lowest energy eigenstates coupled to different photon states of the radiation field, approaching symmetric and antisymmetric superpositions near resonance [14]. These superpositions correspond to the localized states in the case of pyramidal molecules [15].

Case (ii). $\mu_0 = 0, \alpha = 1$ amount to not including the radiation field in the analysis. This gives $z_0 = 0$ or $z_0^2 = \frac{\mu^2 - 1}{\mu^2 + \zeta^2}$. Clearly, this situation corresponds to the Grecchi–Sacchetti proposal [13].

Case (iii). $\mu \neq 0, \zeta \neq 0, \mu_0 \neq 0, z_0 \neq 0 \Rightarrow 0 < z_0^2 < \frac{\mu^2 - \alpha^2}{\mu^2 + \zeta^2}$ or $\frac{\mu^2 - \alpha^2}{\mu^2 + \zeta^2} < z_0^2 < 1$.

For this case, the two inequalities allow nearly localized ($|z_0| \sim 1$) as well as delocalized ($|z_0| \ll 1$) solutions at different values of pressure. To investigate the stability of these stationary solutions, we consider the autonomous system of ordinary differential equations $\dot{z} \equiv f_1(z, \theta)$ and $\dot{\theta} \equiv f_2(z, \theta)$ [16]. Writing $y_1 = z, y_2 = \theta$ and $y_1^0 = z_0, y_2^0 = \theta_0$ the

constant derivatives at the critical point (z_0, θ_0) are given by the matrix F with elements $f_{ij} \equiv \left. \frac{\partial f_i}{\partial y_j} \right|_{(y_1^0, y_2^0)}$:

$$\left. \begin{aligned} f_{11} &= -2\omega\zeta\sqrt{1-z_0^2}\cos\theta_0 \\ f_{12} &= 2\omega\sqrt{1-z_0^2}(\alpha\cos\theta_0 + \zeta z_0\sin\theta_0) \\ f_{21} &= 2\omega\left[\mu - \frac{\zeta z_0\sin\theta_0}{\sqrt{1-z_0^2}} - \frac{\alpha\cos\theta_0 + \zeta z_0\sin\theta_0}{(1-z_0^2)^{\frac{3}{2}}}\right] \\ f_{22} &= 0 \end{aligned} \right\}. \quad (11)$$

Also, the roots λ of the secular polynomial $\det(F - \lambda I) = 0$ are given by

$$\lambda = \frac{f_{11} \pm \sqrt{(f_{11})^2 + 4f_{12}f_{21}}}{2}. \quad (12)$$

For the allowed stationary solutions, it is possible to evaluate numerically the values of the matrix elements f_{ij} using equations (11) and hence to find the roots λ . Depending on the nature of these roots, the stability of the stationary solution can be investigated.

For given values of parameters $(\alpha, \zeta, \mu, \mu_0)$, equation (9) is a polynomial of degree 4 in z_0 . Numerical analysis shows the existence of a critical value of nonlinearity parameter $\mu = \mu_c$, at which bifurcation takes place, i.e. below μ_c , there are only two (real) solutions, one stable and the other unstable which bifurcate into four solutions above μ_c ; two stable and two unstable. Further, as expected, there is a shift in bifurcation point due to the presence of the linear interaction term involving the electromagnetic radiation. In an analysis without electromagnetic radiation, $\mu_c = 1$, whereas in our case μ_c depends on the value of μ_0 , for given values of α and ζ . For instance, for $\mu_0 = 1$, μ_c is approximately 1.7 while for $\mu_0 = 0.1$, μ_c is approximately 0.45. In fact, as μ_0 becomes smaller and smaller, $\mu_c \rightarrow \alpha$. Figure 1 shows the shift in bifurcation point from $\mu_c = 1$ to a value close to α for $\mu_0 = 10^{-4}$.

We can numerically look into some particular solutions and find the required values of Rabi frequency, in the case of, for example, ammonia molecule ($2\omega = 24$ GHz, $P_{cr} = 1.7$ atm) for given values of μ , ζ and α , and for a chosen value of z_0 .

For $\mu = 0.5$ (sub-critical pressure in the absence of molecule–field coupling), $\zeta = 0.2$ and $\alpha = 0.2$, the inequality $\frac{\mu^2 - \alpha^2}{\mu^2 + \zeta^2} < z_0^2 < 1$ allows $z_0 = \pm 0.999$ as a possible solution, which requires $\mu_0 \sim \pm 6$. This implies that a Rabi frequency of about 144 GHz for the interaction of an ammonia molecule with the radiation field of about 19 GHz frequency can localize the molecule at sub-critical pressure. In this case, the roots of the secular polynomial are complex conjugate pairs with negative real part. Hence the corresponding solutions are stable (spiral sinks). It can easily be checked that still lesser values of pressures (μ) require higher and higher values of the Rabi frequency (μ_0) to achieve localization as one would expect. The other inequality allows delocalized solutions which, being unstable (saddle points), are not physically interesting.

The high Rabi frequency requirement for $z_0 = \pm 0.999$ is not a matter of concern. The required Rabi frequency depends sensitively on the localization parameter z_0 and, of course, the detuning parameter α . For example, for $\alpha = 0.1$ and $z_0 = 0.91$, the Rabi frequency is much lower, about 19 MHz. This corresponds to a power requirement in milliwatt range, which is within experimental reach.

For $\mu = 3$ (above critical pressure in the absence of molecule–field coupling), $\zeta = 0.2$, $\alpha = 0.2$, the inequality $0 < z_0^2 < \frac{\mu^2 - \alpha^2}{\mu^2 + \zeta^2}$ allows the choice $z_0 = \pm 0.2$, giving $\mu_0 \sim \mp 0.6$.

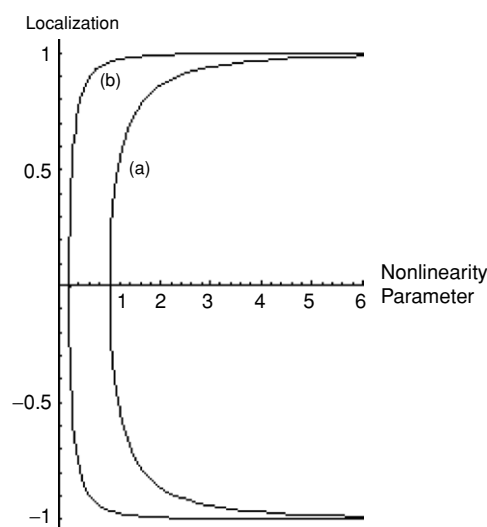


Figure 1. Graph showing the localization parameter (z_0) as a function of the nonlinearity parameter (μ) with $\zeta = 0.2$. Plot (a) refers to the situation when there is no molecule–field coupling [9, 13] and the bifurcation point is $\mu_c = 1$. Plot (b) refers to the situation of the present work where molecule–field coupling is included, and the bifurcation point μ_c depends on the Rabi frequency (and the detuning and dissipative parameters). Plot (b) shown is for $\mu_0 = 10^{-4}$ and $\alpha = \zeta = 0.2$, where the bifurcation point is seen to be close to α .

These nearly delocalized solutions are, however, again unstable (saddle points) and therefore, are not physically significant. On the other hand, the other inequality allows stable nearly localized solutions. This is hardly surprising since stable localized solutions exist in this case even without the radiation field.

Physically, the phenomena explored in this paper are closely related to the quantum Zeno (and anti-Zeno) effect discussed extensively in the literature [17–19]. Reference [18], for example, considered the dynamics of a system subject to an external time-dependent perturbation and a continuous nonselective measurement of some observable. In the present case, the external perturbation is the electromagnetic radiation while the nonlinear interaction of a molecule with the rest of the gas plays the role of an external bath with a non-flat spectrum. Our work then is a specific manifestation of the results of [18] for the problem of the localization of pyramidal molecules.

4. Conclusion

In the present investigation, we have considered stationary states of a pyramidal molecule coupled to an electromagnetic field and interacting with other molecules in the surroundings through dipolar and dissipative interactions. It was found that the nonlinear differential equations for the imbalance variable z and the relative phase variable θ give a polynomial of degree 4 in z representing the condition for (z_0, θ_0) to be a stationary solution. Numerical analysis of this equation shows a shift in the bifurcation point in the solution from its value $\mu_c = 1$ to a value depending on the Rabi frequency and the detuning and dissipative parameters. The consequences of this equation are, as expected, consistent with the limiting cases of no radiation field [9, 13] on the one hand and no molecular environment [14] on the

other. However, our result gives a detailed connection between the values of Rabi frequency, molecular pressure, detuning and dissipative parameters, and the extent of localization achieved for the stationary state. In particular, it gives the value of Rabi frequency needed for localization of a pyramidal molecule for different values of pressure.

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