Molecular localization induced by collisions

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(April 13, 1999)

Abstract

Abstract: We consider a periodically driven double well potential as a dynamical model for molecular localization induced by collisions. If the frequency of the collisions is high enough, we have effective localization, due to the larger instability of one of the metastable states. We show also that the red shift effect of the inversion line can be given by this model.

PACS: 03.65.-w, 33.80.Be, 73.40.Gk, 82.90.+j

In this letter we return on the old problem of the explanation of the *molecular localization* (hereafter ML) hypothesis, successfully used in chemistry as the *molecular structure* concept, in the rigorous quantum mechanics (hereafter QM) framework [1]. QM predicts that stationary states have a distribution probability satisfying the same symmetrical properties of the Hamiltonian; in contrast, ML hypothesis considers molecular states having a shape that drastically breaks the symmetry of the Hamiltonian. The qualitative explanation of this apparent contradiction is simple: the molecule is not an isolated system, and there are no stationary states [2]. The problem is the understanding of the basic effect that makes a simple molecular system to have some macroscopic properties.

In particular, we consider the case of the ammonia molecule, where the model for the motion of the nitrogen atom is given by means of a double well potential with large internal barrier; we expect to observe the pyramidal shape, i.e. the nitrogen atom in one well, with probability 1/2 [1]. Experiments show that the *inversion line*, related to the splitting of the ground state, vanishes (red shift) in the limit of large pressure of the gas and we have the pyramidal shape with full probability. The argument of the vanishing of the splitting (hereafter VS) is theoretically relevant; indeed, localization of a double well stable state, by means of a small static perturbation, is accompanied by the growing of the splitting [3]. Recently, in a joint work, A Martinez and us showed that the ML and VS are both obtained in the case of metastable states [4].

In this paper the instability in the double-well model is generated in a dynamical way by means of a periodically time-dependent external perturbation. The time-dependent perturbation simulates the dynamical influence of the environment on the ammonia molecule, that is the collisions with the other molecules of the gas where the collision frequency is related to the gas pressure. The periodicity is not a natural condition, but is the simplest one and turns out to be compatible with the expected results, at least for a frequency value not too large; in fact, for very high frequencies one should take into account non periodic effects due to the occurrence of less frequent but stronger collisions. The results give the generality of the ML for high frequency and in the simultaneous limit of small perturbation and large barrier between the wells; in particular we have taken the strength of the perturbation proportional to the square root of the splitting. Moreover, by means of a small static perturbation term, which would partially restore the broken symmetry, we make the two Floquet resonances to (anti-)cross. In such a case we obtain the gradual vanishing of the splitting (red shift of the inversion line) at a critical pressure; at this value of the pressure (frequency), we have that the lifetime of the system is of the same order of the beating period.

In order to have explicit results we consider an elementary double well model given by a one-dimensional Schrödinger operator H with a real-valued symmetric double well potential V such that $\lim_{|x|\to\infty} V(x) = 0$. The discrete spectrum of H is given by two negative non-degenerate eigenvalues (energy levels) $\lambda_1 < \lambda_2$ and the continuous spectrum by the real-positive axis. The difference between the two levels gives the small splitting, due to the large barrier between the wells, defined as $\omega = 2\delta$, $\delta = (\lambda_2 - \lambda_1)/2\hbar$. The asymmetrical time-dependent perturbation W, that simultaneously introduces the breaking of the symmetry and the instability of the system, is given by means of a potential periodic in time on one of the wells and vanishing on the other well; that is $W(x,t) = \epsilon v(\mu t) f(x)$ where ϵ is a small real and positive parameter, $v(t)$ is a periodic (kick-type) function with period 2π and $f(x)$ is a real-valued function with compact support contained in one well.

By means of new techniques for the analysis of non-autonomous Hamiltonian systems we compute here the Floquet spectrum of the time-dependent Schrödinger operator $H+W$ with the rigorous control of the error [5]. To this end let the solution of the time-dependent Schrödinger equation $i\dot{\phi} = (H+W)\phi$ be written as

$$\phi(t,x) = a_+(t)\psi_+(x) + a_-(t)\psi_-(x) + \phi_c(t,x), \tag{1}$$

where $\psi_\pm = (\psi_1 \pm \psi_2)/\sqrt{2}$ are the *single-well* states, $\psi_{1,2}$ are the eigenvectors of H associated to the eigenvalues $\lambda_{1,2}$ and $\phi_c = P_c\phi$ where P_c denotes the projection operator on the eigenspace associated to the continuous spectrum of H, that is $\langle \phi_c(t,\cdot), \psi_\pm \rangle = 0$ for any t; $\langle \cdot, \cdot \rangle$ denotes the usual scalar product on the Hilbert space L^2. The substitution of ϕ by (1) leads to the following system of equations

$$\left\{ (Font) LaTeX Font Warning : Command invalid in math mode 1214.5pt c \quad \begin{array}{c} i\dot{a}_+ \\ = \\ \Omega a_+ - \delta a_- + \langle \psi_+, W\phi \rangle \\ i\dot{a}_- \\ = \\ -\delta a_+ + \Omega a_- + \langle \psi_-, W\phi \rangle \\ i\dot{\phi}_c \\ = \\ H\phi_c + P_c W\phi \end{array} \right. \tag{2}$$

where $\Omega = (\lambda_1 + \lambda_2)/2$. Let $\tau = \delta t$ be a *slow time* (in this way the beating period becomes 2π), F be the 2×2 matrix with elements $F_{\pm,\pm} = \langle \psi_\pm, f\psi_\pm \rangle$, $I = s_1$ be the first Pauli matrix, $A(\tau)$ be the column matrix with elements $A_\pm(\tau) = a_\pm(t)e^{i\Omega t}$ and R_c be the column matrix with elements $R_{c,\pm} = \frac{1}{\delta} e^{i\Omega t} \langle \psi_\pm, W\phi_c \rangle$, then the first two equations of the above system can be written as

$$iA'(\tau) = \left[-I + (\epsilon/\delta) v \left(\mu\tau/\delta \right) F \right] A(\tau) + R_c. \tag{3}$$

We remark that in the limit of large barrier between the two wells then $\delta \ll 1$ and the single-well states $\psi_\pm$ are asymptotically given by $\psi_0(\pm x)$, where $\psi_0(x)$ is localized in one well, for instance the right one [6]. If, as we can assume without lack of generality, $f(x)$ has compact support contained in the right well, then it follows that $F_{+,+} \sim f_0 = \langle \psi_0, f\psi_0 \rangle$ and the other terms of F can be neglected in the large barrier limit.

Now, it is a matter of integration by parts and use of the third differential equation of the system (2), to obtain that the remainder term in equation (3) can be arranged as

$$R_c = (\epsilon^2/\delta) U A + R,$$

where U is a 2×2 matrix independent of τ and R is a remainder term obtained collecting the other contributes. As above, in the large barrier limit, we have that

$$U_{+,+} \sim u_0 = -4 \sum_{n \neq 0} |c_n|^2 \Lambda(\Omega + n\mu),$$

where c_n are the Fourier coefficients of $v(t)$, and

$$\Lambda(E) = \langle f\psi_0, [H - (E + i0)]^{-1} P_c f\psi_0 \rangle,$$

the other terms of U can be neglected; we remark that $\Im u_0(\mu) \leq 0$ for any μ and, generically, $\Im u_0(\mu) < 0$ provided that $\Omega + n\mu > 0$ for some n such that $c_n \neq 0$. If we denote $v = v_p + v_0$, where v_0 is the mean value of $v(t)$ in one period, and

$$M = -I + (\epsilon v_0/\delta)F + (\epsilon^2/\delta)U,$$

then (3) takes the form

$$iA'(\tau) = [M + (\epsilon/\delta) v_p (\mu\tau/\delta) F] A(\tau) + R,$$

which has solution

$$A(\tau) = e^{-i(\epsilon/\delta)\int_0^\tau v_p(\mu s/\delta) ds F} \left[e^{-iM\tau} A(0) + R_A(\tau) \right],$$

where $e^{-i(\epsilon/\delta)\int_0^\tau v_p(\mu s/\delta) ds F} = 1 + O(\epsilon/\mu)$, for any τ fixed, since v_p has mean value zero. In order to bound the elements $R_{A,\pm}$ of the remainder term $R_A(\tau)$, in the simultaneous limit of small perturbation and large barrier, we assume the following time-decay behavior for some $s > 1$: $e^{-iHt} P_c \sim O(t^{-s})$ as specified in [7]. Then we can prove that for ϵ small enough and for any τ fixed

$$|R_{A,\pm}(\tau)| \leq (\epsilon^3/\delta) C \max |A_\pm(0)|, \tag{4}$$

for some positive constant C.

Hence, the beating effect between the two wells is completely described by means of the eigenvalues $\ell_{1,2}$ of the matrix M; indeed, from (4) we obtain that

$$A_\pm(\tau) \sim c_{1,\pm} e^{-i\ell_1\tau} + c_{2,\pm} e^{-i\ell_2\tau},$$

for any τ fixed and for some $c_{1,\pm}$ and $c_{2,\pm}$. In the large barrier limit, the leading term of these eigenvalues is given by $\ell_{1,2} \sim \left[u \pm \sqrt{1+u^2}\right]$, where $u = (u_0 k + z)/2$ and where we define $k = \epsilon^2/\delta$ and $z = \epsilon v_0 f_0/\delta$. In the following we assume v_0 small enough (in particular $|v_0| \le \epsilon$); in the opposite case, it follows that the main effect of the perturbation is a drastic destruction of the symmetry and the time-dependent term does not affect the dynamics in a substantial way.

Now, in order to give a more explicit description, we consider the one-dimensional double-well model with piece-wise constant static potential $V(x) = V_1 \chi_{[0,x_1]}(|x|) - V_2 \chi_{(x_1,x_1+a)}(|x|)$, where $\chi_I(x)$ is equal to 1 for any $x \in I$ and 0 otherwise, a, x_1, V_1 and V_2 are positive constants such that the discrete spectrum of H consists of only two eigenvalues; for instance, $a = 5$, $V_2 = 0.25$, $x_1 = 4$ and V_1 large enough such that $\Omega = -0.06932$ and $\delta \ll 1$. For what concerns the perturbation we take $f(x) = \chi_{(x_1,x_1+a)}(x)$ and $v_p(t)$ with Fourier coefficients $c_n = c_{-n} = \frac{\sin(n\pi/N)}{2n/N}(1-(-1)^n)$, $n = 1, \ldots, N$, $c_j = c_0 = 0$, $|j| > N$, we fix $N = 12$. In order to compute the function $\Lambda(E)$, in the large barrier limit, we can use the Dirichlet operator H_D on $L^2(0,+\infty)$ with potential equal to $-V_2$ on the interval $(0,a)$ and zero otherwise. From this and from the fact that f and ψ_0 are real-valued functions it follows that

$$\begin{aligned}\Lambda(E) &\sim \left\langle f\psi_0, [H_D - (E+i0)]^{-1} f\psi_0 \right\rangle \\ &= -\frac{2}{w}\int_0^a f(x)\psi_0(x)u_1(x)dx \int_x^a f(y)\psi_0(y)u_2(y)dy\end{aligned}$$

where u_1 and u_2 are the solutions of the equation $[H_D - (E+i0)]u = 0$ such that $u_1(0) = 0$ and $u_2(+\infty) = 0$, and w denotes the Wronskian [8].

In the case $k \ll 1$, then $\ell_{1,2} \sim \pm 1$ and we still have the unperturbed beating effect. In contrast, for $v_0 = 0$ and k fixed and large enough, i.e. $k \ge k_0$ for some k_0 but such that $\epsilon k \ll 1$ in order to use (4), we obtain the wanted result: that is the beating effect gradually disappears for the frequency μ increasing and larger than a threshold value, in fact we take into account only a finite number of Fourier harmonics of v_p. Indeed, $\Im \ell_1 \sim 0$ and

$\Im \ell_2 \sim k \Im u_0(\mu) < 0$ for μ not too small (see Figure 1a), then we obtain the destruction of the beating effect because the right single-well state rapidly decays, actually it is a metastable state with lifetime shorter than the beating period. In order to consider the contribution given by the static term v_0, we define the minimum splitting value defined for any μ as $\Delta(\mu) = \min_z |\Re(\ell_2 - \ell_1)|$, where $k \geq k_0$ is fixed as above. Then we have the vanishing of $\Delta(\mu)$ for any $\mu > \mu^\star$, as appears in Figure 1b, where $\mu^\star$ is the critical frequency for which we have an exact crossing of the two eigenvalues $\ell_{1,2}$ (see Figure 2b).

In Figures 2a–c we plot the imaginary and real parts of the eigenvalues $\ell_{1,2}$ for three different values of the frequency. For μ equal to the critical value $\mu^\star$ we have the exact crossing (Figure 2b); in such a case we observe a damped beating effect with beating period much greater than the unperturbed one. For μ slightly larger than the critical value $\mu^\star$ we have the vanishing of the real part of the splitting and the imaginary part of $\ell_{1,2}$ is substantially unaffected (Figure 2c); in such a case we have the destruction of beating effect and the localization result. In contrast, for $\mu < \mu^\star$ we have the avoided crossing of the real part of the eigenvalues $\ell_{1,2}$ (Figure 2a) and we found, at the avoided crossing point, the unperturbed splitting value, i.e. $\Delta(\mu)$ close to 2; in such a way we have that the static term v_0 would restore the broken symmetry due to v_p.

We close by underlining that the study of the dynamics of a two-level system under an external time-dependent perturbation is interesting by itself and it appears in many other fields; from the study of spin systems coupled with an environmental sea [9] to the study of quantum transport of electrons in heterostructures modulated by external fields [10], to name but a few. We also recall previous discussions about the possible destruction of the beating (or tunneling) effect [11] in the different limit $\delta \ll \mu \ll \epsilon$, that is for the external frequency going to zero together with the perturbation strength, and for $v(t) = \cos(t)$, for particular values of the ratio ϵ/μ proportional to the zeros of the zero-th Bessel function.

Conclusions: In the present research we have studied a periodically driven double well model in order to understand the large validity of the molecular structure concept. On the basis of our results it is possible that molecular collisions determine (at a critical pressure) a critical instability on a generic beating state which becomes a more stable localized state (definitely stabilized by the polarization of the environment [2] [3]). Moreover, partially restoring the symmetry by means of a small static perturbation, we make the two Floquet resonances to (anti-)cross, so that the splitting vanishes at the critical pressure (red shift of the inversion line). The extension to non periodic perturbations, expected to improve the results for large pressure, will be discussed in a following research.

Acknowledgements: This work is partially supported by the Italian MURST and CNR-GNFM. VG is supported by the INFN and by the University of Bologna (funds for selected research topics); AS is supported by the program "Progetti di ricerca orientata" of the University of Modena.

FIGURES

FIG. 1. In figure (a) we plot the imaginary part of the eigenvalues ℓ_1 (broken line) and ℓ_2 (full line) for $z = 0$ and $k = 50$ fixed and $\mu \in (0.01, 0.016)$, dots line represents the reference value -2. Occurrence of cusps, for the values of $\mu = \Omega/n$ for some n such that $c_n \neq 0$, is a consequence of the fact that the function $\Lambda(E)$ is an analytic function with branch point at $E = 0$ [12]. In figure (b) we plot the minimum splitting value $\Delta(\mu)$, showing the vanishing for any μ larger than the critical value $\mu^\star$. We see that the imaginary part of ℓ_2 is near the value -2 at $\mu = \mu^\star$.

FIG. 2. We plot the real (full line) and imaginary part (broken line) of the eigenvalues $\ell_{1,2}$ for $k = 50$ fixed. For the critical value $\mu = \mu^\star \approx 0.01536$ (figure (b)) we have an exact crossing; vanishing of the real part of the splitting and avoided crossing of the real part of the eigenvalues are observed, respectively, for $\mu > \mu^\star$ ($\mu \approx 0.156$ in figure (c)) and $\mu < \mu^\star$ ($\mu \approx 0.15$ in figure (a)).

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