Molecular localization induced by collisions

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We consider a periodically driven double well as a simplified dynamical model for molecular localization induced by collisions. If the frequency of the collisions is high enough, so that the instability of the states is larger than a critical value, then the states are localized and we have the redshift of the inversion line.

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In this paper we discuss the splitting instability in a periodically driven double well. The physical motivation of this study comes from the relevance of the concept of molecular structure in chemistry, but the model could be tested directly by means of heterostructures and microwaves. Let us recall the old problem of the explanation of the molecular localization (ML) hypothesis, successfully used in chemistry as the concept of molecular structure, in the rigorous quantum-mechanics (QM) framework [1]. QM requires that the probability distribution of stationary states have the same symmetry of the Hamiltonian, in marked contrast with the ML requirement. The qualitative explanation of this apparent contradiction is simple: since the molecule is not an isolated system, its states cannot be stationary [2]. The main problem is the understanding of the quantitative aspect of the phenomenon, as it results from the following question by Woolley [1]: ''Why should the general quantum theory describing energy eigenstates turn out to be of such little use in chemistry, or put in another way, why should transitions out of the time-dependent molecular quantum states which empirically appear to be an essential ingredient of any useful quantum chemistry, be so slow?''

Although it is generally accepted that the phenomenon should be explained by means of decoherence arguments [3], it is also clear that explicit models are needed. Thus, by means of the study of an explicit model, we want to point out the role of instability in the localization phenomenon. Indeed, we expect the existence of metastable states in perturbed systems and we want to study the smallness of the interaction between a pair of such states for large instability. Let us consider the case of the ammonia molecule NH_3, where the model for the motion of the nitrogen atom N is a double well with a large internal barrier [1]. In this model we have the pyramidal shape of the molecule (molecular structure) if the state is localized in one of the wells. The *inversion line* of the molecular microwave emission gives the energy splitting of the stationary states. Experiments on ammonia gas show that the localization and the *inversion line* are dependent on pressure. In particular, the localization probability increases and the *inversion line* broadens and decreases as the pressure increases, giving the so-called redshift (RS) effect [2].

Some previous explicit models [4] which are able to explain ML, are autonomous, i.e., they make use of time-independent potentials. In particular in a recent paper [5], by using an unstable autonomous model, both ML and RS are obtained.

In the present paper we use a nonautonomous model (time-dependent potential) so that the instability caused by the molecular, collisions is represented in a more realistic way.

In particular, our model consists of a double-well potential with a time-dependent perturbation simulating the dynamical influence of the environment on the ammonia molecule, i.e., the collisions with the other molecules of the gas, where the collision frequency is related to the pressure. Let us notice that the present model is more physical than the previous ones for the reasons stated above, but it is still simplified. One simplification is the choice of a perturbation periodic in time. This choice is technical and is due to the recent improvement of methods for handling periodic problems. We point out that the classical resonance effect between different frequencies are not relevant for the results. In any case the results give an *a posteriori* justification of the model.

Since the first (but not the second) order perturbation term vanishes, we set the perturbation of the same order of the square root of the splitting. We consider the large internal barrier regime, so that both the splitting and the perturbation are exponentially small. This choice of parameters is similar to previous ones, and allows us to apply the same comparison with experiments given by Claverie and Jona Lasinio [4], although in that case the frequency parameter was absent. If the periodic perturbation is strong enough, and the Fourier coefficients are slowly decreasing for increasing index, we have localization for a frequency larger than a critical value but smaller than a large value. This upper bound should be related to the simplification of the model given by the periodicity of the time behavior. Since the model is linear, we have no spontaneous symmetry breaking, so that the perturbation is asymmetric, but not too much, in order to have the RS. We control the asymmetry of the perturbation by varying the coefficient of the time independent perturbation.

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Let us notice that both effects, i.e., localization and the vanishing of the splitting, occur at a critical frequency giving a critical instability, such that the mean life of the states is the same of the unperturbed beating period. In this case the width of the inversion line is of the same order of the unperturbed line itself.

We consider a one-dimensional Schrödinger operator H with a real-valued symmetric double-well potential V such that the discrete spectrum of H is given by two negative nondegenerate eigenvalues (energy levels) $\lambda_1<\lambda_2$ and the essential spectrum by the positive real axis. The difference between the two levels gives the splitting defined as $\omega=2\delta$, $\delta=(\lambda_2-\lambda_1)/2\hbar$; in the following, for the sake of simplicity, we take $\hbar$ fixed and equal to 1. 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 nonautonomous Hamiltonian systems we compute here the solutions of the time-dependent Schrödinger equation $i\dot{\phi}=(H+W)\phi$ with the rigorous control of the error [6]. To this end, let the solution of the time-dependent Schrödinger equation be written as

$$\phi(t,x)=a_+(t)\psi_+(x)+a_-(t)\psi_-(x)+\phi_c(t,x), \qquad (1)$$

where $\psi_\pm=(\psi_1\pm\psi_2)/\sqrt{2}$ are the *single-well* states, $\psi_{1,2}$ are the normalized 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 essential 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 $L^2(R)$. The substitution of ϕ by Eq. (1) leads to the following system of equations:

$$\begin{aligned} i\dot{a}_+&=\Omega a_+-\delta a_-+\langle\psi_+,W\phi\rangle,\\ i\dot{a}_-&=-\delta a_++\Omega a_-+\langle\psi_-,W\phi\rangle,\\ i\dot{\phi}_c&=H\phi_c+P_cW\phi, \end{aligned} \qquad (2)$$

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 $R_{c,\pm}=(1/\delta)e^{i\Omega t}\langle\psi_\pm,W\phi_c\rangle$; then the first two equations of the above system can be written as

$$iA'(\tau)=[-I+(\epsilon/\delta)v(\mu\tau/\delta)F]A(\tau)+R_c, \qquad (3)$$

where $'$ denotes the derivative with respect to τ.

We remark that in the limit of large barrier between the two wells then $\delta\ll1$ and the single-well states $\psi_\pm$ are asymptotically given by $\psi_0(\pm x)$, where $\psi_0(x)$ is localized in one well [7]. If, as we can assume without lack of generality, $f(x)$ has compact support contained in the same 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 system (2), to obtain that the remainder term in Eq. (3) can be arranged as

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

where U is a 2×2 matrix with elements $U_{\pm,\pm}$ independent of τ and R is a remainder term obtained collecting the other contributions. In particular, in the large barrier limit we have that

$$U_{+,+}\sim u_0=-4\sum_{n\neq0}|c_n|^2\Lambda(\Omega+n\mu),$$

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

$$\Lambda(E)=\langle f\psi_0,[H-(E+i0)]^{-1}P_cf\psi_0\rangle, \qquad (4)$$

and the other terms of U can be neglected. We remark that $\mathrm{Im}\,u_0(\mu)\leqslant0$ for any μ and, generically, $\mathrm{Im}\,u_0(\mu)<0$ provided that $\Omega+n\mu>0$ for some n such that $c_n\neq0$. 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 Eq. (3) takes the final form

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

which has solution

$$A(\tau)=e^{-i(\epsilon/\delta)\int_0^\tau v_p(\mu s/\delta)dsF}[e^{-iM\tau}A(0)+R_A(\tau)], \qquad (5)$$

where $e^{-i(\epsilon/\delta)\int_0^\tau v_p(\mu s/\delta)dsF}=1+O(\epsilon/\mu)$, for any τ, since v_p has mean value zero. In the simultaneous limit of small perturbation and large barrier and assuming the time-decay behavior $e^{-iHt}P_c\sim O(t^{-s})$, for some $s>1$, as specified in Ref. [8], we have the following estimate of the remainder term:

$$|R_{A,\pm}(\tau)|\leqslant(\epsilon^3/\delta)C\max|A_\pm(0)|, \qquad (6)$$

for any τ fixed and some positive constant C independent of ϵ and δ.

From Eqs. (1), (5), and (6) it follows that the beating effect between the two single-well states is completely described by means of the eigenvalues $\nu_{1,2}$ of the matrix M; in particular, from Eqs. (5) and (6) we obtain that

$$A_\pm(\tau)\sim c_{1,\pm}e^{-i\nu_1\tau}+c_{2,\pm}e^{-i\nu_2\tau}, \qquad (7)$$

for any τ fixed and for some $c_{1,\pm}$ and $c_{2,\pm}$. The leading term of these eigenvalues is given by $\nu_{1,2}\sim[u\pm\sqrt{1+u^2}]$, where $u=(u_0k+z)/2$ and where we define $k=\epsilon^2/\delta$ and $z=\epsilon v_0f_0/\delta$. In the following we assume v_0 small enough (in particular $|v_0|\leqslant\epsilon$ in order to have z of the same order of k);

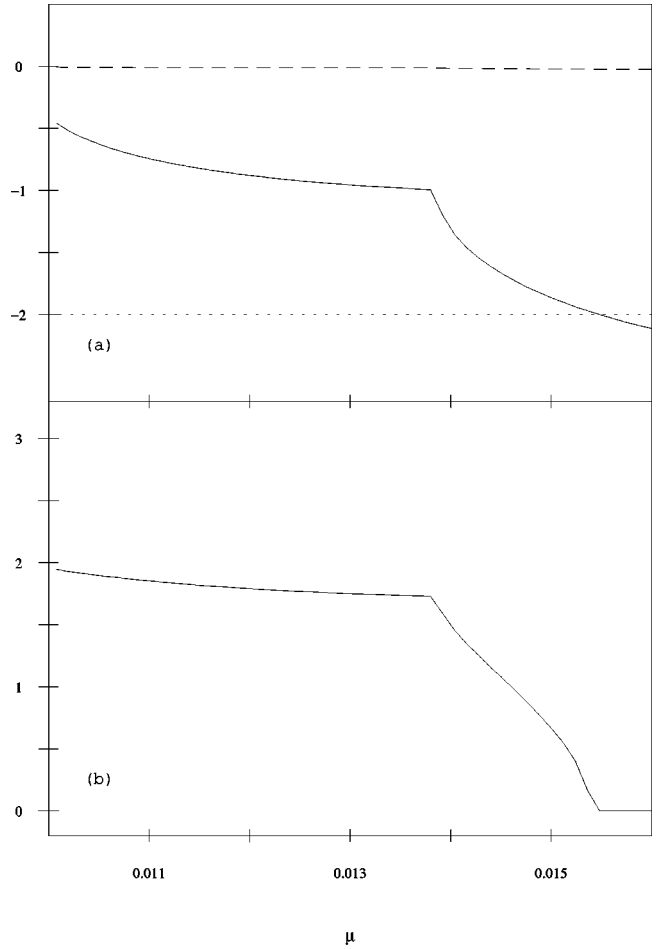

FIG. 1. In (a) we plot the imaginary part of the eigenvalues ℓ_1 (broken line) and ℓ_2 (full line) for $z=0$ and $k=50$ fixed and $\mu \in (0.01,0.016)$, the dotted line represents the reference value -2. The occurrence of cusps, for the values of $\mu=\Omega/n$ for some n such that $c_n \neq 0$, is a consequence of the fact that the function $\Lambda(E)$ is an analytic function with branch point at $E=0$ [14]. In (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 $\mu=\mu^\star$.

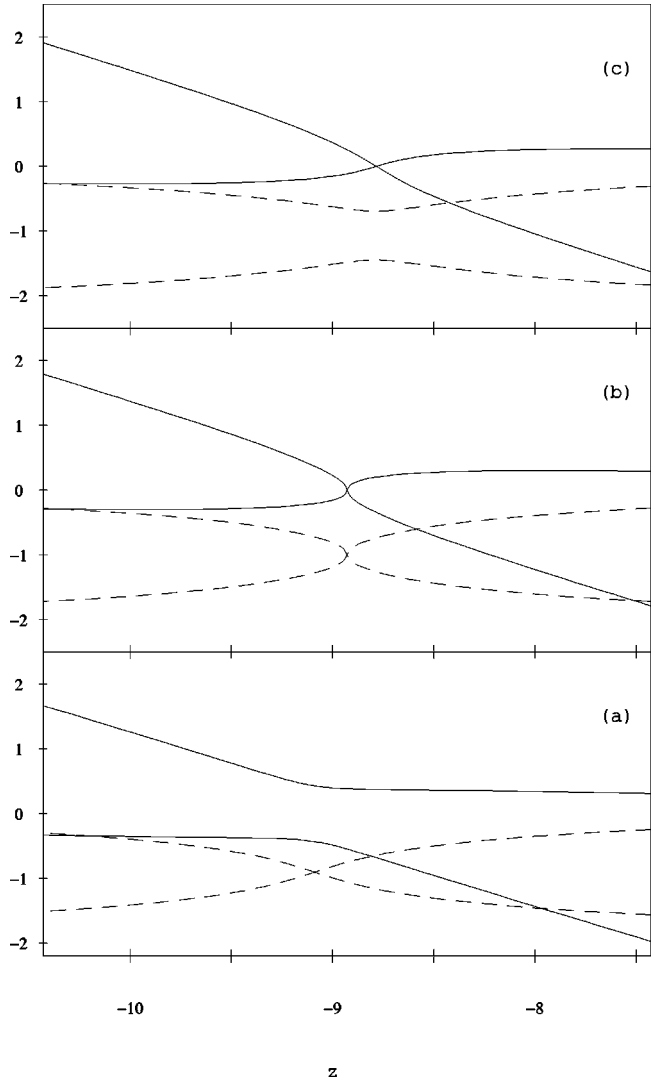

FIG. 2. We plot the real (full line) and imaginary part (broken line) of the eigenvalues $\ell_{1,2}$ for $k=50$ fixed. For the critical value $\mu=\mu^\star \approx 0.015\,36$ (b) we have an exact crossing; vanishing of the real part of the splitting and avoided crossing of the real part of the eigenvalues are observed, respectively, for $\mu>\mu^\star$ [$\mu \approx 0.156$ in (c)] and $\mu<\mu^\star$ [$\mu \approx 0.15$ in (a)].

in the opposite case, it follows that the main effect of the perturbation W is a drastic destruction of the symmetry and the time-dependent term, given by $\epsilon f(x) v_p(t)$, does not affect the dynamics in a substantial way.

Now, in order to obtain an explicit result, we consider a simple one-dimensional double-well model with piecewise constant static potential $V(x)=V_1\chi_{[0,x_1]}(|x|) - V_2\chi_{(x_1,x_1+a)}(|x|)$, where $\chi_S(x)$ is equal to 1 for any $x \in S$ 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 example, for $a=5$, $V_2=0.25$, $x_1=4$, and V_1 large enough, we have that $\Omega=-0.069\,32$ 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 $c_n=c_{-n} = [\sin(n\pi/N)/(2n/N)][1-(-1)^n]$, $n=1,\ldots,N$, $c_j=c_0=0$, $|j|>N=12$. Here, we use dimensionless units. In order to compute the function $\Lambda(E)$ we introduce 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 the fact that f and ψ_0 are real-valued functions and from Eq. (4) it follows that

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

in the limit of large V_1, 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 [9].

The result of the computation is that, in the case $v_0=0$ and $k \ll 1$, 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., $k \geqslant k_0$ for some k_0 but such that $\epsilon k \ll 1$ in order

to use Eq. (6), we obtain the wanted result: that is the beating effect gradually disappears for increasing frequencies μ and larger than a threshold value, in fact we take into account only a finite number of Fourier harmonics of v_p. Indeed, $\mathrm{Im}\,\ell_1 \sim 0$ and $\mathrm{Im}\,\ell_2 \sim k\,\mathrm{Im}\,u_0(\mu) < 0$ for μ not too small [see Fig. 1(a)]; from this fact and from Eq. (7) the destruction of the beating effect follows. In order to consider the contribution given by the static term v_0, we define the minimum splitting value defined for any μ as $\Delta(\mu) = \min_z |\mathrm{Re}(\ell_2 - \ell_1)|$, where $k \geqslant k_0$ is fixed as above. Then we have the vanishing of $\Delta(\mu)$ for any $\mu > \mu^\star$, as it appears in Fig. 1(b), where $\mu^\star$ is the critical frequency for which we have an exact crossing of the two eigenvalues $\ell_{1,2}$ [see Fig. 2(b)].

In Figs. 2(a)–2(c) we plot the imaginary and real parts of the eigenvalues $\ell_{1,2}$ for k fixed as above and for three different values of the frequency. For μ equal to the critical value $\mu^\star$ we have the exact crossing [Fig. 2(b)]; 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 [Fig. 2(c)]; in such a case we have the destruction of the beating effect and the localization result. In contrast, for $\mu < \mu^\star$ we have the avoided crossing of the real part of the eigenvalues $\ell_{1,2}$ [Fig. 2(a)] and we found, at the avoided crossing point, the unperturbed splitting value, i.e., $\Delta(\mu)$ close to 2; in such a way the broken symmetry, due to v_p, would be restored by the static term v_0.

Finally, we quote previous relevant results on localization and destruction of tunneling [10] in the case of a periodic monochromatic external perturbation of a quartic double-well potential. In such a case we have the absence of instability of the states because the double-well potential goes to infinity as x goes to infinity. A periodically driven double-well potential giving the instability of the states has been considered in order to study the role of electron localization in molecular ionization [11]. We underline also that the study of the dynamics of a two-level system under an external time-dependent perturbation is interesting in itself and it appears in many other fields; to name just a few, we mention the study of spin systems coupled with an environmental sea [12] and the study of quantum transport of electrons in heterostructures modulated by external fields [13].

In this paper we have shown that localization and the shrinking of the splitting can be facilitated by instability, generated by a periodic perturbation. Although we are far from the full explanation of the molecular localization effect, some of our predictions can be verified on heterostructures with microwaves perturbations. Further research in progress involve nonperiodic and nonlinear perturbations.

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