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Instability of tunneling and the concept of molecular structure in quantum mechanics: The case of pyramidal molecules and the enantiomer problem

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In this paper we propose a possible explanation of the fact that certain molecules exhibiting symmetric configurations are localized in one of them, instead of being delocalized as predicted by a naive application of quantum mechanics. Our mechanism is based upon the instability, in the semiclassical regime, of delocalized states under small perturbations (among which we consider the reaction field due to the environment). This mechanism predicts, for example, a different behavior for NH_3 and AsH_3 (*delocalized* ground state in the former case, *localized* ground state in the latter case), and similar to the case of AsH_3 we expect localized states in the case of optical isomers, in agreement with the empirical evidence. Possible consequences concerning the understanding of the "classical limit" in general are briefly outlined.

I. INTRODUCTION

In recent years the problem of the compatibility of the classical concept of molecular structure with quantum mechanics has been recognized as a nontrivial one and has received considerable attention in the literature.[1–31] References 1, 7–9, 13, 14, 22, 23, and 28 provide a number of relevant references.

The basic difficulty consists of the fact that the *complete* molecular Hamiltonian (namely, the one involving all electronic *and nuclear* coordinates, not just the electronic ones) exhibits the usual continuous symmetries (translational and rotational invariance), and in addition often admits some "internal" discrete symmetry group. Therefore, according to the general principles of quantum theory, the *complete molecular eigenstates* should belong to some representation of this symmetry group and consequently they should be "delocalized" with respect to the degrees of freedom corresponding to these symmetries. In the present work, we shall consider the internal symmetries only (a typical example is the inversion coordinate in the case of pyramidal molecules, which will be dealt with extensively below). Such a delocalization property is at variance with the usual chemical view, which considers a molecule as an object localized at each instant of time with respect to all its nuclear degrees of freedom (translational, rotational, and internal): This is the concept of "classical molecular structure," as already considered in previous works.[23,24] Hence the problem: how to reconcile the two conflicting pictures (the quantum "delocalized" one and the classical "localized" one). The purpose of this paper is to contribute towards the solution of this problem.

It is now appropriate to introduce the typical example to be used all along in this paper, namely the so-called "inversion symmetry" which occurs in pyramidal molecules of the type XY_3 (Refs. 32 and 33) [e.g., ammonia (NH_3), phospine (PH_3), arsine (AsH_3)]: The potential energy takes the same value for two configurations corresponding to symmetric positions ($x = x_0$ and $x = -x_0$) of the X nucleus (and of the electrons) with respect to the plane determined by the three Y nuclei (see Fig. 1). To be more precise, we may place ourselves in the framework of the Born-Oppenheimer approximation, namely, solving the electronic Hamiltonian for fixed positions $(R_1, \ldots, R_\nu, \ldots, R_N)$ of the nuclei, and then using the (lowest) electronic energy $E_0(R_1, \ldots, R_N)$ as a potential energy for a purely nuclear Hamiltonian. Then, when the nucleus X is constrained to move in a plane parallel to that of the three Y nuclei, we expect a (local) energy minimum when X lies at the intersection of the plane with the ternary symmetry axis corresponding to the three Y nuclei. If we restrict the motion of X to this privileged

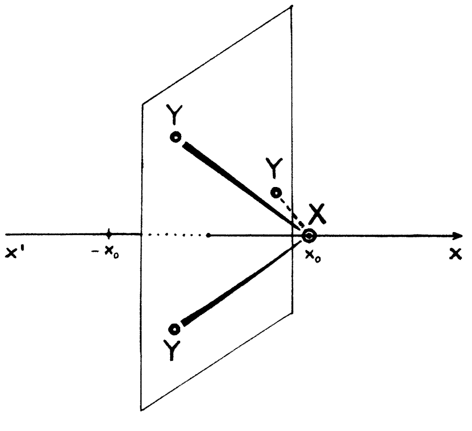

FIG. 1. A pyramidal molecule XY_3 with its inversion axis $x'x$ and the two nuclear equilibrium configurations $-x_0$ and x_0.

axis (taking it as the x axis, say), the potential energy will exhibit a *maximum* when X lies in the Y_3 plane, and two minima (symmetric with respect to this plane) corresponding to the pyramidal "equilibrium" configurations; we thus recognize the framework of a one-dimensional symmetric double-well problem. An exact treatment (going beyond the Born-Oppenheimer approximation) would be more complicated, but, as concerns the inversion symmetry, we expect that the one-dimensional motion along the "inversion coordinate" x should exhibit the essential features of the problem at hand, which may be summarized as follows: while *classically* we have two localized equivalent configurations (at $x=-x_0$ and $x=x_0$) with the same energy (degeneracy), the *quantum-mechanical* treatment gives us two symmetrically delocalized eigenstates $\psi_0(x)$ and $\psi_1(x)$ (see Fig. 2: ψ_0 is symmetric and ψ_1 is antisymmetric, hence both $|\psi_0|^2$ and $|\psi_1|^2$ are symmetric).[33] This quantum-mechanical delocalization may be viewed as a consequence of the possibility of tunneling through a potential barrier with a finite height. Facing the problem of these conflicting aspects between the classical and quantum descriptions, essentially the following two attitudes have been taken so far.

(1) To start from a strict quantum-mechanical theoretical basis and to develop the theory more thoroughly than has been done until now, for quasiclassical conditions, with the hope that some conceptual improvement will come out from this effort. This first attitude has been advocated noticeably by Woolley,[1-8,9(c)] Primas,[10-14] Pfeifer,[15-19] and Lévy-Leblond.[34]

(2) To consider that the conceptual structure of present-day quantum theory is so radically different from the outlook of classical physics that it prevents one from recovering the latter when starting from the former. As a consequence, recovering the classical level of physics would require some modification and/or extension of present quantum theory. This second attitude has been explored in connection with the problems of theoretical chemistry by Julg and Julg,[29,35] Claverie and Diner,[23,36] Claverie,[24,37] and Julg.[30] It may be mentioned that these attempts partly relied upon a tentative stochastic model for microphysics known as stochastic electrodynamics which, despite its conceptual interest, has finally been recognized as defective, at least in its present form (references may be found in Sec. V of Ref. 23 and in the very extensive review by de la Pena[38]).

The present paper may be considered as a contribution to the first line of thought. We shall argue in fact that, in the semiclassical limit, due to the high instability of the delocalized eigenstates under the effect of very small perturbations,[39-43] one should expect that pyramidal molecules with a sufficiently high potential barrier exhibit, as a rule, localized eigenstates under the inevitable perturbing effect of the surroundings. Of course, the same conclusion would apply, in general, to the so-called enantiomer molecules (optical isomers), since they are endowed with very high potential barriers with respect to the transition between the various enantiomer forms.

The point of view taken in this paper is not completely new as several authors have considered the effect of the environment as a possible source of symmetry breaking. Let us point out, therefore, some novelties of the present approach. We do not make at the start a two-state approximation of the double well, but the full-space structure of the molecule is considered. To obtain localization we invoke "universality" of tunneling instability when the splitting becomes very small. By this we mean that in a semiclassical limit "any" perturbation above a certain threshold, even if concentrated in a small space region compared with the size of the molecule, is capable of producing localization. In this way we can decide, essentially on first principles, when a perturbation is going to produce a significant amount of localization. We then look for a perturbation endowed with a universal character and we identify the following one: if a molecule gets localized by a fluctuation, the reaction of the neighboring molecules to the local symmetry breaking tends to stabilize it. The question then arises of whether such a reaction is sufficiently strong to produce the desired effect. Since this type of reaction field, as we shall argue later, does not depend very much on the specific molecule considered, the crucial physical parameters become the closeness of the system to the semiclassical conditions, as measured by the ratio of energy-level splitting due to tunneling to the ground-state energy, and the ratio of the same splitting to the perturbation energy. It is in this respect that we find that NH_3 and AsH_3 are very different molecules to the extent that we expect localization only for AsH_3.

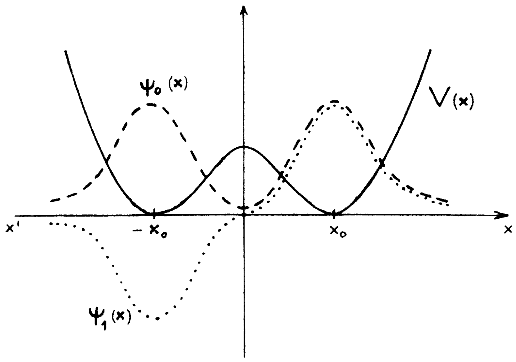

FIG. 2. The one-dimensional symmetric double-well problem. ——, potential $V(x)$; — — —, ground-state eigenfunction $\psi_0(x)$; . . . ., first excited state eigenfunction $\psi_1(x)$.

We now explain the connection between our point of view and the previous works on the subject. The papers of Anderson[44] and Margenau[45] are probably the first to deal with the role of the environment on the inversion spectrum of NH_3. However, their interest is mainly directed towards interpreting the inversion spectrum of NH_3 when the pressure increases and deals only marginally (Anderson) with the localization problem. Furthermore, Anderson deals with the limiting case of high electric fields which corresponds to high pressures. Accordingly, these authors content themselves with a much less refined representation of the environment than our own; namely, they consider the effect of only one or two fixed molecules nearby the one under study, while we use a *reaction field* (see Sec. IV) which aims at representing the average value of the genuine stochastic electric field created by the full real molecular environment.

TABLE I. Experimental and calculated properties of ammonia (NH_3), phosphine (PH_3), and arsine (AsH_3).

	NH_3	PH_3	AsH_3
$(E_1-E_0)_{V_0}{}^{a}$ (10^{-9} a.u.)	3595	1.520×10^{-10}	1.185×10^{-14}
$E_0{}^{b}$ (10^{-9} a.u.)	16.125×10^{6}	11.208×10^{6}	10.065×10^{6}
ρ^{c}	3.65	16.87	20.93
μ^{d} (Debye)	1.47	0.58	0.20
$\epsilon-1$	0.0072	0.002 59	0.002 01
$\mathscr{E}_R{}^{e}$ (10^{-9} a.u.)	44.83	6.559	1.780
$V_1{}^{f}$ (10^{-9} a.u.)	-12.96	-0.748	-0.070
$\lvert V_1\rvert/(E_1-E_0)_{V_0}$	0.361×10^{-2}	4.92×10^{9}	5.91×10^{12}

[a] Energy splitting as evaluated in Ref. 54.

[b] From column ν_1 of Table I in Ref. 54.

[c] Semiclassical parameter defined by Eq. (5).

[d] Dipole moment from Ref. 61.

[e] Reaction electric field according to Eq. (7).

[f] Perturbation potential due to the reaction field [Eq. (8)]. Conversion factors: 1 Debye=0.393 460 a.u. (dipole moment); 1 cm^{-1} $\Leftrightarrow$ $2.997\,884\times10^{-10}$ Hz.

A rather general scheme to describe the interaction of a molecular system with its environment was proposed by Davies.[46] His approach leads to a nonlinear Schrödinger equation as a result of this interaction, with the ensuing possibility of a symmetric breaking. We feel that our approach is very close in spirit to his. However, no explicit application was considered by him.

A different approach, a dynamical one, is taken in the papers by Harris and Stodolsky[47] while both static and dynamical aspects are present in the work of Bixon.[48] (Dynamical aspects of a different nature, which, however, could also become relevant in our context, have been studied in Refs. 49—51.) The conclusion of all these works is that the interaction with the environment should facilitate localization. However, these models involve some phenomenological parameters whose identification and quantification is not immediate.

The treatment of the environment based upon a simple reaction-field model proposed in this paper allows one to use only physical parameters such as pressure, temperature, dielectric constants, etc. In this way we can make easy numerical estimates of the perturbing potential V and compare them with the inversion splittings ΔE of the molecules under consideration. The very large variation of the ratio $V/\Delta E$ (see Table I) between NH_3 and AsH_3 (or PH_3) together with the theory of tunneling instability mentioned before, allows one to interpret the differences in behavior of these two molecules. Furthermore, it suggests the possibility of some kind of phase transition from a quantum behavior to a semiclassical one associated with the inversion degree of freedom of such molecules.

Finally, the results thus obtained for the "inversion coordinate" suggest that similar developments could be attempted for other degrees of freedom (e.g., rotation, translation), with the purpose of shedding a new light upon the problem of the "classical limit" of quantum theory.

II. INSTABILITY OF TUNNELING UNDER SEMICLASSICAL CONDITIONS

In the present section we briefly recall the phenomenon of the instability of tunneling under semiclassical conditions. This problem was first investigated by using stochastic methods,[40] and later on through more standard tools of functional analysis.[42,43]

Let us consider a symmetric double-well potential $V_0(x)$, and let us add to it a perturbing potential $V_1(x)$ localized inside one of the wells but possibly away from the minimum (see Fig. 3). More precisely, $V_1(x)$ fulfills the conditions

$$\begin{aligned} &V_1(x)>0 \quad \text{for } x\in(a_1,a_2)\subset(0,x^*)\ , \\ &V_1(x)=0 \quad \text{otherwise}\ , \end{aligned} \tag{1}$$

where x^* is larger than 1 (see Refs. 39 and 40 for details). Then, "practically independent" of the strength of the perturbation (see below for a more quantitative statement),

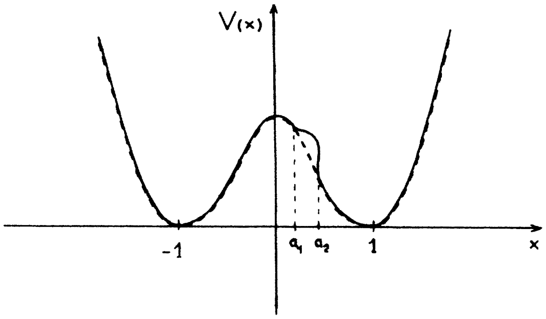

FIG. 3. A symmetric double-well potential with a local perturbation. ——, perturbed potential $V(x)=V_0(x)+V_1(x)$; — — —, unperturbed potential $V_0(x)$. The x axis has been scaled so that the absolute value x_0 of the minima is equal to 1.

the following estimate holds for sufficiently small $\hbar/m$ (m denotes the mass of the particle):

$$\frac{\psi_0(1)}{\psi_0(-1)} \approx -\frac{\psi_1(-1)}{\psi_1(1)} \approx \exp\left[-\frac{1}{\hbar}\int_{-a_2}^{a_2}[2mV_0(x)]^{1/2}dx\right], \quad (2)$$

where $\psi_0(x)$ and $\psi_1(x)$ denote, respectively, the ground state and the first excited state corresponding to the *perturbed* problem. The remarkable consequence of this estimate is that a localized perturbation is sufficient for producing an exponential rate of localization of the wave function, and moreover, this exponential rate depends only on the position of the perturbation. A similar estimate shows that the splitting of the two lowest eigenvalues also increases by an exponential factor as a consequence of the perturbation; we actually have

$$\frac{(E_1-E_0)_{V_0}}{(E_1-E_0)_{V_0+V_1}} \approx \frac{\exp\left[-\frac{2}{\hbar}\int_0^1[2mV_0(x)]^{1/2}dx\right]}{\exp\left[-\frac{2}{\hbar}\int_{a_2}^1[2mV_0(x)]^{1/2}dx\right]} = \exp\left[-\frac{2}{\hbar}\int_0^{a_2}[2mV_0(x)]^{1/2}dx\right], \quad (3)$$

where $(E_1-E_0)_V$ denotes the splitting corresponding to the potential V. The "independence" of these estimates from the intensity of the perturbation V_1 holds provided the latter fulfills the following condition:

$$|V_1| \gg \exp\left[-\frac{C(a_2)}{\hbar}\right], \quad (4)$$

where $C(a_2)=2\int_0^{a_2}[2mV_0(x)]^{1/2}dx$. This is a very weak requirement indeed: it means, for example, that a perturbation of order $\hbar^\alpha$, α being an arbitrary positive number, would produce the above effects in the limit $\hbar \rightarrow 0$; in practice it means that a small but fixed perturbation will produce these effects if $(mV_0)^{1/2}(\Delta x/\hbar)$ becomes large enough, which will commonly happen because V_0, or m, or both become large [here $V_0=V_0(0)$ denotes the height of the potential barrier, and Δx denotes its width].

The meaning of the above result is that, in the real world, the localization of the wave function in a double well should be the rule under the conditions of the semiclassical limit. It is already well known that changing the curvature of one of the two symmetric minima would produce localization in the well with the smallest curvature. The above result shows that essentially "any" perturbation has the same effect. To be sure, it is possible to show that, by perturbing the potential at several places in a suitable way, one can destroy the symmetry of the potential while maintaining delocalization.[52] However, this requires such a fine tuning of these various local perturbations that such a case must be considered physically as highly improbable and unstable.

We finally come to a very important point: what do we mean by "semiclassical conditions"? It is clear that, in any given physical situation, $\hbar$ keeps a well-defined value, while the mass m and especially the height $V_0(0)$ of the potential barrier change from one system to the other. Thus, the relevant feature of the semiclassical domain is the exponential smallness of the splitting $(E_1-E_0)_{V_0}$ (evaluated for the symmetric potential V_0) as compared with the separation (of order $\hbar\omega$) of the vibrational levels inside each potential well. Since the ground-state energy E_0 is very nearly equal to $\hbar\omega/2$, it will be natural to take for the semiclassical parameter ρ the expression:

$$\rho = \left|\log_{10}\left[\frac{E_1-E_0}{E_0}\right]_{V_0}\right|, \quad (5)$$

where the subscript V_0 means that the quantities E_0 and (E_1-E_0) are evaluated for the symmetrical situation [corresponding to the potential $V_0(x)$].

III. PYRAMIDAL MOLECULES

In this section we want to examine the consequences of the previously developed considerations in the case of pyramidal molecules such as ammonia (NH_3), phosphine (PH_3), arsine (AsH_3), and their substituted derivatives (which could possibly exhibit optical activity when the three substituents are different). It is known that these compounds behave experimentally in different ways:[53,54] in the case of ammonia, it is easy to observe spectroscopically the splitting $(E_1-E_0)_{V_0}=0.7935\ \mathrm{cm}^{-1}$ between the two *delocalized* states ψ_0 and ψ_1 (generated by the possibility of tunneling between the two localized pyramidal configurations), and, accordingly, it is difficult to find substituted derivatives which exhibit optical activity (such compounds are obtained only when the substituents generate a high enough potential barrier between the two possible configurations); on the contrary, for arsine, the splitting $(E_1-E_0)_{V_0}$ would be so small that it could not be observed with any conceivable experimental technique; we indeed have two reasonably close evaluations of this splitting, based upon data concerning the usual vibrations in each potential well: $3.7\times10^{-18}\ \mathrm{cm}^{-1}$ (Costain and Sutherland[53]) and $2.6\times10^{-18}\ \mathrm{cm}^{-1}$ (Weston[54]), corresponding to the extremely small transition frequencies 1.109×10^{-7} Hz and 0.78×10^{-7} Hz, respectively. In actual fact we shall argue that this transition does not exist at all, because the corresponding *delocalized* states ψ_0 and ψ_1 themselves do not exist any more, being replaced by localized states. In agreement with this lack of the "inversion transition," optically active compounds involving trivalent arsenic have actually been found.[53,54] In the case of phosphine, due to the use of somewhat different values as concerns the geometry of the equilibrium pyramidal configuration [length of the P—H bond = 1.46 Å (Ref. 53) or 1.415 Å (Ref. 54), respectively], Costain and Sutherland[53] on one hand, and Weston[54] on the other hand found very different values for the energy splitting $(E_1-E_0)_{V_0}$: $4.76\times10^{-4}\ \mathrm{cm}^{-1}$ (corresponding to 1.4277×10^{7} Hz) and $3.336\times10^{-14}\ \mathrm{cm}^{-1}$ (corresponding to 10^{-3} Hz), respectively. Such a large discrepancy illustrates the high sensitivity of the splitting with respect to the height of the potential barrier, due to the exponential character of the formula giving $(E_1-E_0)_{V_0}$ [see Eq. (1) in Ref. 54 and Eq.

(3.8) in Ref 39]. The later evaluation by Weston[54] should be more reliable, since his geometry is the one accepted nowadays,[55(a)] and we therefore retained it in the present work. Thus phosphine appears as an intermediate case between ammonia and arsine, but closer to the latter (its splitting has not been experimentally observed[53,54] which implies that it would certainly be much smaller than that for ammonia).

From our present point of view, the relevant fact is that ammonia and arsine are very different as concerns their situation with respect to the semiclassical regime. Indeed, if we evaluate the parameter ρ according to Eq. (5) by using the values of (E_1-E_0) recalled above [see also our Table I and the values of E_0 borrowed from Weston[54] (column ν_1 in Table I of this paper)], we get the values

$$\rho(\mathrm{NH_3})=\left|\log_{10}\left[\frac{0.79}{3539}\right]\right|=3.65\ , \tag{6a}$$

$$\rho(\mathrm{AsH_3})=\left|\log_{10}\left[\frac{2.6\times10^{-18}}{2209}\right]\right|=20.93\ . \tag{6b}$$

Therefore arsine lies much deeper in the semiclassical region than ammonia [as concerns phosphine, Weston's values would give $\rho(\mathrm{PH_3})=\log_{10}(3.336\times10^{-14}/2460)=16.87$, which would mean a strong semiclassical character, too]. According to the discussion of the previous section, this means that ammonia and arsine should behave very differently with respect to external perturbations such as those due to neighbor molecules. More precisely, a molecule $\mathrm{NH_3}$ should be rather insensitive to perturbations as concerns the symmetry breaking (see, e.g., the evaluations in Sec. VI G of Ref. 23), while a molecule $\mathrm{AsH_3}$ should very often appear localized with respect to its inversion coordinate (symmetry very easily broken).

IV. REACTION-FIELD MODEL OF THE ENVIRONMENT

At this point, it is important to realize that, if we deal with a physical set of molecules (e.g., in the gaseous state), once localization happens for a molecule such as $\mathrm{AsH_3}$, *there appears a cooperative effect which tends to stabilize this localization.* The mechanism is the following: once a molecule is in a (localized) nonsymmetric state, it has a nonzero average dipole moment $\boldsymbol{\mu}=\langle\boldsymbol{\mu}\rangle$ (where $\boldsymbol{\mu}$ denotes the dipole moment operator); then this moment locally polarizes the surrounding which, in turn creates, at the position of $\boldsymbol{\mu}$, a so-called *reaction field* $\mathcal{E}_R$, which is collinear with $\boldsymbol{\mu}$, so that the interaction $-\boldsymbol{\mu}\cdot\mathcal{E}_R$ is negative and hence tends to stabilize the nonsymmetric state under consideration; indeed, according to the results[39–43] summarized in Sec. II, the localization occurs on the side where the potential energy is lowered by the perturbation (strictly speaking, we should use as an effective interaction energy with the surroundings the *free energy* of interaction,[56] namely,[57] $-\frac{1}{2}\boldsymbol{\mu}\cdot\mathcal{E}_R$, which changes nothing essential). The reaction field is nothing but the statistical mechanical average $\langle\mathcal{E}\rangle$ of the electric field $\mathcal{E}$ created by the molecules surrounding the dipole $\boldsymbol{\mu}$, and it is a very standard topic in the theory of the dielectric constant and of the solvent effects.[57–59] This is clearly a nonlinear effect, since the perturbing reaction potential depends on the state of the molecule through the average value $\langle\boldsymbol{\mu}\rangle$, and in this respect our approach is in agreement with Davies's[46] and Yomosa's[60] schemes.

It seems appropriate to emphasize here that the reaction field depends only on rather global properties of the surrounding medium (dielectric constant and cavity radius in our model), and not at all upon the detailed states of the molecules of which this medium is made. Noticeably, if we consider a pure substance, namely the surrounding molecules which are themselves pyramidal and have an inversion coordinate, no assumption is needed concerning whether these molecules are in delocalized (symmetrical) or localized (unsymmetrical) states; as strongly emphasized by Woolley (Ref. 1, Sec. V), the dielectric constant of the medium has practically the same value in any case. Consequently, when the specific molecule that we consider becomes localized (due to some external perturbation) and thereby acquires a nonzero average dipole moment, we get the corresponding reaction field even if all surrounding molecules are in their delocalized state: thus *no circular reasoning is involved* (the situation would be different if we had to assume that the surrounding molecules already are in a localized state in order to generate the reaction field).

A. Numerical estimates

Now the essential question is whether the reaction field that we can expect in such a physical situation is sufficiently large for triggering the localization mechanism discussed in Sec. II. In order to deal with this question, we shall use, as in the previous work[23] (Eq. IV 27) the well-known expression[59(a)] of the reaction field $\mathcal{E}_R$ corresponding to a dipole $\boldsymbol{\mu}$ embedded in a spherical cavity of radius a inside a medium with dielectric constant ε:

$$\mathcal{E}_R=\frac{2(\varepsilon-1)}{2\epsilon+1}\frac{\boldsymbol{\mu}}{a^3}\ , \tag{7}$$

which gives for the perturbation potential

$$V_1=-\tfrac{1}{2}\boldsymbol{\mu}\cdot\mathcal{E}_R=-\frac{(\varepsilon-1)}{2\epsilon+1}\frac{\mu^2}{a^3} \tag{8}$$

in cgs or a.u. $[1/(4\pi\epsilon_0)=1]$.

We shall first describe how our values of the quantities μ, α, and ϵ are chosen, and afterwards we shall give some physical discussion concerning the model thus obtained. We shall consider our three compounds ($\mathrm{NH_3}$, $\mathrm{PH_3}$, $\mathrm{AsH_3}$) under standard conditions ($T=0\,^\circ\mathrm{C}$, $P=1$ atm), all three then being in the gaseous state (boiling temperatures under $P=1$ atm being, respectively:[55(b)] $-33.55\,^\circ\mathrm{C}$; $-87.7\,^\circ\mathrm{C}$; $-55\,^\circ\mathrm{C}$). From the normal molar volume $V_{\mathrm{mol}}=22\,414$ cm^3, and the Avogadro number $N=6.023\times10^{23}$, we get the volume per molecule $v_{\mathrm{mol}}=V_{\mathrm{mol}}/N=37\,214\times10^{-24}$ cm^3, and by requiring that the volume of the spherical cavity of radius a is equal to v_{mol}, we get [taking 1 a.u. (length)$=0.529\,17$ Å]

$$a^3=\frac{3}{4\pi}\frac{V_{\mathrm{mol}}}{N}=8\,884.2\ \text{Å}^3=59\,956\ (\text{a.u.})^3\ . \tag{9}$$

The values of the dipole moments (see Table I) were taken from the table of Nelson *et al.*[61] Finally, as concerns the dielectric constant ε, we used for NH_3 the experimental value[55(c)] $\epsilon=1.0072$, while for PH_3 and AsH_3, we evaluated ϵ from the Clausius-Mossotti-Debye equation:[59(b)]

$$\frac{\epsilon-1}{\epsilon+1}V_{\text{mol}}=\frac{4\pi}{3}N\left[\alpha+\frac{\mu^2}{3k_BT}\right], \tag{10}$$

where $\alpha=\alpha_e+\alpha_a$ (α_e denotes electronic polarizability, α_a denotes atomic polarizability), k_B denotes the Boltzmann constant, and all other quantities have already been defined. This formula gives quite satisfactory results for gases,[59] as we actually checked for NH_3: using $\alpha_e=2.16$ Å^3 (from Ref. 62), hence $(4\pi/3)N\alpha_e=5.45$ cm^3, and $(4\pi/3)N\alpha_a=0.75$ cm^3 (Ref. 63), we obtained $\epsilon-1=0.007\,328$, in satisfactory agreement with the above quoted experimental value $\epsilon-1=0.0072$. Then, we took the experimental data[64] for PH_3,

$$T=16.0\,^\circ\text{C}\ ,\quad P=756\text{ mm Hg}\ ,\quad \varepsilon-1=0.002\,38\ ,$$

and for AsH_3,

$$T=16.0\,^\circ\text{C}\ ,\quad P=762\text{ mm Hg}\ ,\quad \varepsilon-1=0.001\,92$$

and, using the known values of μ (see Table I), we determined the following values for the term $(4\pi/3)N\alpha$ in Eq. (10): For PH_3,

$$(4\pi/3)N\alpha=11.80\text{ cm}^3\ ,$$

and for AsH_3,

$$(4\pi/3)N\alpha=14.31\text{ cm}^3\ .$$

Then, from Eq. (10), we got the desired values of $(\varepsilon-1)$ at $T=0\,^\circ$C and $P=760$ mm Hg: For PH_3,

$$\epsilon-1=0.002\,59\ ,$$

and for AsH_3,

$$\epsilon-1=0.002\,04\ .$$

We now discuss briefly the accuracy of our reaction-field model. First of all, as pointed out above, the reaction field is only the (time or ensemble) average of the instantaneous electric field created by the environment, the fluctuations of this field (which would be needed in order to perform a detailed kinetic study) are outside the scope of this model. Second comes the question of the parameters, essentially the value of the cavity radius a, since the values of μ and ϵ are well defined. It is clear that the value [about 20 Å according to Eq. (9)] derived from the volume per molecule V_{mol}/N may be taken as an order of magnitude only, since this radius is about ten times larger than the molecular radius proper, the spherical cavity will not remain permanently empty, we shall always find some of the surrounding molecules passing through it in the course of time. This would suggest that our cavity model, which discards these occurrences of intermolecular distances shorter than the cavity radius a, may underestimate the average field. An argument in favor of this guess is provided by the influence of the pressure on the experimental inversion spectrum of NH_3:[45] under 1 atm, this spectrum is already severely disturbed, while our evaluation of the reaction field gives a perturbation V_1 markedly smaller than the splitting (E_1-E_0), which would suggest a weak perturbation of the inversion spectrum. But already our (possibly underestimated) value of the reaction field for AsH_3 (and PH_3) gives a clearcut result for these molecules, namely $|V_1|\gg(E_1-E_0)$ (with the ensuing localization); a larger value of the reaction field would only reinforce this conclusion. In actual fact, for these molecules the orders of magnitude of $|V_1|$ and of $(E_1-E_0)_{V_0}$ are so different, due to the smallness of the latter, that even a very rough evaluation of the former is sufficient for drawing a nonambiguous conclusion.

B. Physical consequences: localization versus delocalization

From these values of μ, $(\epsilon-1)$, and a^3, we could evaluate from Eq. (8) the values of the perturbation potential V_1 due to the reaction field, and these values are displayed in Table I, together with the values of the splittings $(E_1-E_0)_{V_0}$ to which they must be compared. Indeed, according to the discussion in Sec. II, the minimal requirement for localization is $|V_1|\gg|(E_1-E_0)_{V_0}|$, since this corresponds to condition (4) for $a_2=1$, which means a perturbation acting at the minimum (which is the most efficient position). In actual fact, our perturbation (namely the reaction field) is not strongly localized and we may, therefore, hope that the minimal requirement above is a reasonable criterion. The result of this comparison is quite striking: when going from ammonia to arsine, $|V_1|$ decreases by 2 orders of magnitude (from 10^{-8} to 10^{-10} a.u.), while $(E_1-E_0)_{V_0}$ decreases by 18 orders of magnitude (from 10^{-5} to 10^{-23} a.u.), so that we have $|V_1|/(E_1-E_0)_{V_0}\ll 1$ for NH_3 and $\gg 1$ for AsH_3. It is clear that even if we had adopted a criterion more severe than the "minimal requirement" above, the contrast between NH_3 and AsH_3 would be maintained. Therefore, for AsH_3, which according to (6b) is definitely semiclassical, the "cooperative" effect of the other molecules (manifesting itself through the reaction field acting on each molecule) may result in the stabilization of the localized states in the course of time. Note that, as mentioned above, when evaluating the reaction field due to a polar molecule, it is immaterial whether the surrounding molecules are in localized or delocalized states, since the dielectric constant of the medium is essentially the same in any case, as emphasized by Woolley (Ref. 1, Sec. V). By the way, let us mention that it is possible to construct simple statistical models which indicate that a true phase transition might be involved in the problem under consideration.

By contrast, in the case of NH_3, $|V_1|$ remains small with respect to the inversion splitting (at least under reasonably low pressure), and we therefore expect that the delocalization states will persist in the presence of the usual surroundings. As concerns PH_3, Weston's value[54] for $(E_1-E_0)_{V_0}$ reported in Table I leads to $|V_1|\gg(E_1-E_0)_{V_0}$, which implies that, under the standard conditions considered, this molecule should, like

AsH_3, be localized with respect to the inversion coordinate. It is clear that the above discussion raises the problem of the *transition* between the genuine quantum behavior and the semiclassical behavior for *some* degrees of freedom (essentially the nuclear ones) in molecules. In particular, by considering intermediate situations between those of ammonia and arsine, we may wonder whether, under suitably varying conditions of pressure and temperature, it would be possible to realize the switching from one regime to the other, which would appear as some kind of phase transition. Indeed, $(E_1-E_0)_{V_0}$ is a characteristic of the individual molecule, while V_1 depends on the environment; according to Eq. (9), $a^3 \propto V_{\text{mol}}$, and, according to Eq. (10), $(\epsilon-1)\propto 1/V_{\text{mol}}$, hence, according to Eq. (8),

$$|V_1| \propto 1/(V_{\text{mol}})^2=(P/RT)^2 \,. \tag{11}$$

Let us now consider the case of phosphine. According to Table I, we have (for normal conditions $T=0\,^\circ\text{C}$ and $P=760$ mm Hg) $|V_1|/(E_1-E_0)_{V_0}\simeq 0.5\times 10^{10}$; then, we should bring this ratio to the value 1 by reducing the pressure through a factor 10^{-5} namely by taking $P\simeq 10^{-3}$ to 10^{-2} mm Hg, which seems quite feasible. The transition from the quantum (delocalized) regime to the classical (localized) one should manifest itself through the disappearance of the "inversion" transition line (and of other spectroscopic features) related with the existence of the "inversion delocalized" states such as ψ_0 and ψ_1. To be sure, in the case of phosphine the transition frequency $(E_1-E_0)_{V_0}/h=10^{-3}$ Hz seems too small to detect even indirectly (moreover, the low pressure required would reduce the absorption coefficient and therefore make spectroscopic detection more difficult), and anyway, with such a small value of $(E_1-E_0)_{V_0}$, other factors may still alter the picture [e.g., the interaction with the electromagnetic vacuum field, as proposed by Pfeifer (Ref. 15, Sec. 10; Refs. 16—19); see conclusion below]. However, by searching intermediate cases between ammonia and phosphine (e.g., by replacing H atoms by bulkier substituents in NH_3), we could expect to find some better candidates for the experimental observation of the expected "quantum to semiclassical transition." For example, indirect evaluation of the barrier height from experimental data (vibrational force constants and molecular geometrical parameters)[54] actually gives for $N(CH_3)_3$ a value intermediate between those of NH_3 and PH_3 (see Table II), and, on another hand, according to quantum chemical computations,[65,66] the same situation should hold for the other two molecules NH_2F and NCl_3 (see Table II). Consequently, further work (both theoretical and experimental) concerning such molecules appears desirable, in order to investigate the possibility that they would exhibit the transition from quantum (delocalized) regime to classical (localized) regime under suitable physical conditions.

Let us mention that the transition mechanism that we propose might be only weakly cooperative, so that the transition would not be very sharp; but this is not an essential point, since the main problem is rather to account for the appearance of such different states as the delocalized and the localized ones, under correspondingly different appropriate conditions.

TABLE II. Inversion barriers of NH_3, PH_3, AsH_3, and $N(CH_3)_3$, NH_2F, NCl_3.

	Barrier (kcal/mole)	
Compound	Experimental	Computed
NH_3	6.00[a]	5.9[d]
	5.93[b], 5.78[c]	9.01 (2.04)[e]
PH_3	17.45[a]	36.8[f,g]
	27.4 (31.8)[b]	38.0 (35.0)[h]
		42.09 (31.94)[e]
AsH_3	32.09[a]	46[i]
	35.0[b]	
$N(CH_3)_3$	8.19[b]	
NH_2F		20.16 (13.0)[e]
NCl_3		22.9 (24.1)[j]

[a] Reference 53. The barrier estimated for PH_3 is certainly too low, as discussed by Weston (Ref. 54).

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Finally, as concerns the so-called enantiomer molecules (optical isomers), they are endowed with *very high* potential barriers, and correspondingly with *extremely small* values of the splitting (E_1-E_0) (in the case of the amino acid alanine, for example, Pfeifer[15] proposes the value 10^{-70} a.u.). Under such conditions, the mechanism proposed in the present work is obviously operative and therefore accounts for the existence of the (optically active) localized enantiomer states instead of the symmetrical (optically inactive) delocalized state.

V. CONCLUSION

In the present work, by using (1) the notion of the high instability of delocalized states (in a symmetric double-well potential) under semiclassical conditions and their propensity to give rise to localized states under fairly arbitrary perturbations, and then by invoking (2) a special perturbation endowed with a *systematic* character (nonzero average), namely the reaction field due to the environment, we have been able to propose a rather definite scheme concerning the appearance of some features pertaining to the concept of classical molecular structure, namely well-defined (localized) configurations with respect to some (nuclear) degrees of freedom.

It is appropriate to recall here that Pfeifer (Ref. 15, Sec. 10; Refs. 16—19) also invoked a phase transition analogy in the framework of his own work concerning the localization of certain molecular degrees of freedom due to the interaction of the molecule with the *electromagnetic vacuum field* which is introduced in quantum electrodynamics.

As a somewhat related topic, we may notice that Prat[67] proposed an interpretation of atomic valency (namely the property of forming chemical bonds according to a well-defined geometrical scheme) as a result of breaking the (spherical) symmetry of the (isolated) atom through its interaction with the environment (the type of symmetry breaking, namely the possible resulting subgroups of the full rotation group, should of course depend on the atomic species under consideration). The common feature with our own problem which deserves to be mentioned is the capability of the environment to elicit a *response (symmetry breaking) whose characteristics depend on the subsystem itself and not at all upon the detailed structure of the environment.* Two other proposals concerning the occurrence of symmetry breaking for electronic (rather than nuclear) wave functions may be quoted here: the so-called sudden polarization effect[68] and the appearance of unsymmetrical electronic states for some molecules in polar solvents.[60] It seems worth emphasizing that, in the latter case,[60] the author proposes a *nonlinear "effective" wave equation* for determining the unsymmetrical state, just as done in the previously quoted work of Davies,[46] who dealt with a quite different specific problem. This methodological convergence well illustrates the very general character of the conceptual framework under consideration, namely the symmetry breaking in appropriate quantum systems (e.g., symmetric double-well potential) as a result of the interaction with their environment.

It may finally be mentioned that Woolley[2,5,6] had also considered the possibility that the interaction of an individual molecule with its environment could play an instrumental role in the appearance of the classical features of the usual concept of molecular structure, but his proposal was essentially of a qualitative nature (Ref. 23, end of Sec. IV E). We can also quote in this respect a very recent work by Joos and Zeh,[69] who try to give a more precise content to this idea, namely the emergence of classical properties through interaction with the environment; following a line of thought akin to that of Harris and Stodolsky[47] and of Simonius,[70] these authors aim at justifying the vanishing of nondiagonal "interference" terms of the reduced density matrix pertaining to the subsystem under consideration, with the purpose of accounting for the appearance of "localized" classical-type states instead of the "delocalized" genuine eigenstates pertaining to a fully isolated subsystem. Their proposed schemes are, at the present stage, of a rather general and abstract nature. By contrast, the scheme proposed in our present work initially concerns a specific problem (symmetrical double-well systems), and it can therefore exhibit a much more definite nature (this scheme indeed introduces usual well-defined physical parameters and discusses their role in terms of actual numerical values). Accordingly, when compared with other attempts, the present work should significantly contribute towards answering the questions raised, for example, in a previous paper (Ref. 23, Sec. IV G) about the generation and maintenance (in the course of time) of localized states pertaining not only to the inversion coordinate (as considered in the present work), but to other degrees of freedom as well (e.g., rotational and translational ones). Developing such a general scheme would, in our opinion, enable us to understand the so-called transition to the classical limit in a much more thorough and physical way than has been achieved through the treatments proposed until now.

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