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Citation: *J. Chem. Phys.* **102**, 337 (1995); doi: 10.1063/1.469407

View online: <http://dx.doi.org/10.1063/1.469407>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v102/i1>

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# How robust are molecular properties? A stability criterion for eigenstates

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(Received 1 June 1994; accepted 19 September 1994)

We propose a stability criterion applicable to eigenstates of approximate Hamiltonians. We define a “robustness” of the physical properties of the underlying system under a variety of internal and external conditions that can be deduced from stability properties of the eigenstates of the approximate Hamiltonian. Stability properties are assigned to an ensemble of eigenstates according to the statistics of its response to an ensemble of random perturbations of given magnitude. The stability criterion is explicitly formulated for the eigenstates of polyatomic molecules exhibiting a normal to local mode transition. As an example, a stability analysis for the water molecule is carried out and experiments in the low density gas phase (rotational energy transfer), high density gas phase (collision-induced spectra), and condensed phase are suggested. © 1995 American Institute of Physics.

## I. INTRODUCTION

The experimentally recorded spectrum of resonant frequencies provides the primary source of information about a quantum system. The first step of the theoretical analysis consists in comparing the spectrum to a prediction from the molecular Hamiltonian. However, such a comparison on the basis of the exact Hamiltonian is often impractical and not instructive. Therefore, one commonly resorts to an approximate Hamiltonian that can be obtained in two conceptually different ways. First, it can be derived from the exact Hamiltonian by successive simplifications based on physical assumptions about the relative magnitudes of the various contributions; second, the approximate Hamiltonian can be postulated as an algebraic form satisfying various symmetry requirements and conservation laws, i.e., a power series in terms of, by assumption good, quantum numbers and their corresponding ladder operators. Then expansion parameters are determined such that computed and observed spectra agree up to the order of magnitude of the neglected contributions. Common to both schemes is that the search for dominant terms is guided by their effect on the spectrum. Further steps in the theoretical analysis are based on such approximate Hamiltonians, and require the computation of the eigenstates.

However, the approximate eigenstates that are obtained in this manner are not necessarily accurate approximations to the exact eigenstates, i.e., a small correction to an approximate Hamiltonian, small enough to be invisible in the spectrum to given accuracy, may produce a set of profoundly different eigenstates. Then the expectation values of operators other than the approximate Hamiltonian, e.g., the dipole moment operator, the polarizability operator, ..., may vary significantly under the same correction that leaves the spectrum invariant. These variations may not only differ from operator to operator, but also for a particular operator from eigenstate to eigenstate. Furthermore, if an eigenstate tends to change significantly under a particular small correction to the approximate Hamiltonian, then there may as well be other corrections of comparable magnitude that induce similar changes.

From the instability of the eigenstates of the approximate Hamiltonian under small corrections, we conclude that the eigenstates of the approximated exact Hamiltonian may vary profoundly under comparable small perturbations of the system. Therefore the instability of approximate eigenstates hints at a genuine physical property of the modeled system.

In order to discuss the different aspects of the instability of physical properties of quantum systems we make the following proposition: *We call a physical property or a state of a quantum system robust if it does not change significantly on average under a variety of internal and external conditions.*

The notion of robustness becomes important in many standard chemical research problems, e.g., if one seeks a molecule with a particular physical property that needs to be robust under a given variety of conditions, or if one seeks the variety of conditions that allows a particular physical property of a given molecule to be robust. One may even be interested in the cases where the opposite is true.

Let us briefly explain the meaning of the single phrases used in the definition of robustness.

Internal conditions may be specified by the degrees of freedom that are excited, e.g., rotational, vibrational, or electronic degrees of freedom, the interactions between various degrees of freedom, e.g., rotational–vibrational coupling, vibrational–electronic coupling, ..., and the initial conditions of excitation.

External conditions may be specified by the interaction of the molecule with its surroundings, e.g., short range interactions, like collisions, or field mediated interactions, such as electromagnetic interactions, and the internal conditions of the surroundings.

The change of any physical property, such as dipole moment and polarizabilities, under varying internal or external conditions can be directly obtained from changes in the eigenstates. The significance of an observed change lies in the eye of the beholder and may be measured by setting an agreed-upon threshold, e.g., one may agree that it is significant if the dipole moment of a molecule changes by more than half of its value under the conditions *A* when the conditions vary to *B*.

The “average over a variety of conditions” can be understood in two ways, dependent on whether the conditions are of deterministic or probabilistic nature. For example, consider molecules of the same species embedded in an inhomogeneous solid matrix. Each molecule is in a different local environment. If we are interested in the dipole moment of the molecular species coarse grained over the solid, we could determine the dipole moment of each single molecule in its particular environment and then take an average over all the molecules in their different local environments, i.e., the various external conditions. Now suppose that each of local environments is subject to changes, say distortions by vibrational excitations of the solid matrix, that can have an impact not only on the type of the perturbation of the molecule, but also the strength of perturbation. Then each of the particular local conformations of the environment for a single molecule has to be weighted by the probability of the distortion to occur. That is, the total average takes account of the deterministic effect of each particular local environment and the probabilistic effect of each particular distorted environment to occur. This variety of microscopic conditions can be expressed in terms of parameters that specify the macroscopic state of the solid matrix, e.g., temperature, pressure,... . Then, even a further average over a range of those parameters may be taken.

The issue of robustness becomes important in the following general scenarios: (1) *molecules in highly excited states* display couplings between the degrees of freedom with a wide range of coupling strengths. In the representation of the small couplings, the particular choice of a Hamiltonian must appear as arbitrary, i.e., as good as any other representation of comparable coupling strength. Then it is important to investigate the changes in the eigenstates upon change from one Hamiltonian to another, i.e., upon change from one assumed internal condition to an energetically comparable one. (2) *Molecules coupled to a field* display a large number of couplings that are mediated by the field. Such a field may be present in the form of the inhomogeneous solid matrix, as discussed above, or in the form of electromagnetic radiation. Again, there may be a large degree of arbitrariness in the representation of the field in the molecular Hamiltonian. Thus, the robustness under a change from one external condition to another must be demonstrated in order to obtain a valid representation of the eigenstates. As we show in this paper, these effects become most apparent if the symmetry of the system is lowered upon a small perturbation.

Although it is possible to address the issue from a general point of view, the present investigation is carried out in the framework of a longstanding issue in molecular vibrational spectroscopy: the normal to local mode transition in polyatomic molecules. The class of  $AB_2$  molecules with  $C_{2v}$  symmetry, such as the water molecule, will provide an example, from which we will deduce a generalization to other classes of symmetric and nonsymmetric polyatomic molecules.

The approximate Hamiltonian that correctly generates the vibrational spectrum of the water molecule is called the Darling–Dennison Hamiltonian.<sup>1</sup> In the second quantized representation, it is an algebraic form in the raising and low-

ering operators for the *normal* modes. Henry and Siebrand<sup>2</sup> found that an algebraic form in the raising and lowering operators of the *local* modes shows an at least equally good agreement with the spectrum; the agreement is even excellent for the low energy states within the same overtone manifold. The normal to local mode transition can be associated with an increasingly better overlap of eigenstates with local mode basis states. That result could be extended to other types of polyatomic molecules and opens the discussion as to the *physical nature* of these vibrational states. For a comprehensive review and bibliography on the topic, the reader is referred to Ref. 3. Attention has been focused on models of identical harmonically coupled local bond Morse oscillators, both classical and quantum mechanical. These are especially appealing from a physical point of view and lead directly to the local mode expansion.

The quantum mechanical aspects of the normal to local mode transition were studied by Stannard *et al.*<sup>4</sup> and then in a series of detailed investigations by Child and Lawton.<sup>5</sup> *Local character* was attributed to states that appear in pairs split by an energy difference small compared to the energy difference to neighboring states in the spectrum, *normal character* to all other states. The splitting between pairs of states of local character was attributed to tunneling between degenerate states of local character. Some important observations can be summarized as follows: states of local character containing  $n$  vibrational quanta usually appear at low energies within the “ $n$ th polyad” and states of normal character at high energies. The number of states of local character within the  $n$ th polyad increases with  $n$ . Weak coupling, strong anharmonicity, and high excitation favor local character states. These observations can be understood and quantified from the properties of a dynamical double well potential using semiclassical ideas.<sup>6</sup>

Quantum mechanical and classical aspects of the normal to local mode transition for  $AB_2$  molecules with  $C_{2v}$  symmetry were also discussed by Sibert *et al.*<sup>7</sup> based on the physical picture of a hindered rotor.

A decisive step towards the reunification of the local and normal picture was made when Lehmann,<sup>8</sup> Kellman,<sup>9</sup> and Mills and Robiette<sup>10</sup> demonstrated the equivalence of the normal Darling–Dennison Hamiltonian and the local algebraic Hamiltonian, which are related by a  $SU(2)$  transformation. Xiao and Kellman<sup>11</sup> proposed a classification scheme for the vibrational states in terms of the *dynamical properties of the classical correspondent* to the quantum mechanical Darling–Dennison Hamiltonian. Their numerical study of phase space trajectories for different molecules shows that the locality or normality of a classical trajectory is *independent of the representation in a local or normal basis*. The display of the classical phase space trajectories of states in the same polyad on the “polyad phase sphere” spanned by  $SU(2)$  coordinates allowed them to assign *unambiguously* the label of local or normal character. Recently the analytical forms of the trajectories were found and the condition for the classical normal to local mode transition was formulated,<sup>6</sup> which is in agreement with earlier results.<sup>12</sup>

At this point, the distinction between the terms *local* and *local character* must be emphasized. Classical local modes

can be assigned to quantum mechanical states of local character. Yet, in contrast to the possibility of localization of excitation in the classical local modes, the quantum mechanical modes of local character are characterized by *delocalization* of excitation in *any* basis. The reason is that all eigenstates are invariant under the molecular symmetry operations. Thus, in the local mode representation, eigenstates are formed by a superposition of two local states of identical excitation and are thus inherently of *nonlocal* nature. Truly local quantum mechanical states can always tunnel between equivalent configurations.

Progress was made by the demonstration<sup>6</sup> of the equivalence of the classical dynamics of exchange of vibrational excitation between bond oscillators to that of an undriven Duffing oscillator<sup>13</sup> without damping. The associated Duffing potential  $V$  can change form from a single well to a double well upon excitation. The normal to local mode transition was connected to that change via a bifurcation parameter  $\kappa$  that not only relates the antagonistic tendencies of transfer and localization, but also takes the total excitation into account. A necessary condition for the transition from normal modes to local modes was that these tendencies are balanced, i.e.,  $|\kappa|=1$ . The physical picture that emerges from this work is that the vibrational excitation moves as a quasiparticle, i.e., as a unit of the “bare” excitation accompanied by a distortion of the molecular equilibrium configuration. This distortion is induced by the excitation and in turn supports the confinement of the excitation by lowering its potential energy. When the excitation is transferred between two oscillators, the overall distortion of the molecular configuration is minimal, i.e., the potential energy of the excitation reaches a maximum and consequently its kinetic energy reaches a minimum. If the kinetic energy of the excitation vanishes at that point the normal to local mode transition occurs.

In an earlier investigation,<sup>14</sup> the difference in the physical properties between eigenstates of local and those of normal character was demonstrated. Quantum states with local mode correspondents in a classical description are extremely susceptible to symmetry-breaking perturbations. When a small symmetry breaking perturbation, such as an energy mismatch between the local oscillators is added to the Hamiltonian, these states *become localized* by mixing. States with normal mode correspondents in a classical description *remain delocalized* when the *same* perturbation is added to the Hamiltonian. Thus it was shown that the susceptibility to symmetry-breaking perturbation is very much larger in local character quantum states than in normal character quantum states. Two quantitative measures for localization exist in these molecules. The *effect* that was measured was formulated in terms of an *order parameter* that indicates the mismatch in occupation numbers of the two local oscillators. The *sensitivity* was measured in terms of a *susceptibility* that indicates the magnitude of minimum perturbation necessary to lead to a significant change in the order parameter. States of low susceptibility may be called “robust” since the change in the expectations of operators other than the Hamiltonian can be expected to be negligible under a small perturbation. In turn, states of high susceptibility may be called “nonrobust.”

Note that the existence of nearly degenerate states, i.e., eigenstates with a small energy splitting, is neither necessary nor sufficient for any state to be highly susceptible. However, it may cause in particular cases a spectacularly high value of the susceptibilities of the associated states if those states are of opposite parity. These high values distract the attention from the issue at the core of the problem, i.e., the change of the eigenstates occurring to orders of perturbation magnitudes where the energy spectrum does not change at all. Therefore an explanation of the normal to local mode transition cannot be based solely on the properties of the eigenvalue spectrum. The power of the method was demonstrated by an application to experimental data for the water molecule. Here it was proven that states of opposite parity appear as nearly degenerate, which could be inferred from the existence of a dynamic double well potential discussed above. Note that, in turn, states of high susceptibility may indicate for more complex molecules the existence of dynamic potentials.

Three problems associated with the earlier procedure remain.

First, the choice of a specific symmetry breaking perturbation appears to be rather arbitrary and artificial. Since stability must prevail under any possible perturbation, the strategy to eliminate arbitrariness is to choose the most effective case. This requires that a chosen perturbation be shown most effective, even in cases where a particular choice seems intuitively clear. For example, in the water molecule, the most effective localizing perturbation is achieved by directly removing the symmetry through an imposed energy mismatch on the two local oscillators. Still, that most effective perturbation may be artificial in the sense that it is forbidden under the particular experimental conditions.

Second, for more complex molecules, the choice of the most effective perturbation may not be obvious, especially if there is a variety of symmetry restrictions or conservation laws for the states and processes.

Third, even in unsymmetric systems, one may observe susceptible states. This can easily be seen if one views the slightly perturbed symmetric system as the unsymmetric original to be perturbed. The most effective perturbation there will be the one that restores symmetry.

This leads directly to the issue of the stability of the eigenstates of the *perturbed* system whose susceptibilities in turn must be evaluated. If, e.g., at the classical normal to local mode transition, the normal modes become unstable when simultaneously the local modes become stable, does this imply that the symmetric eigenstates become unstable and simultaneously the local eigenstates become stable against any perturbation? In order to answer that question, we are forced to repeat the procedure of adding a small arbitrary specific perturbation and evaluating the response. The response is going to depend on the specific choice of perturbation. It can be shown that the perturbed states in turn are as susceptible to a symmetry restoring perturbation as the unperturbed states are to a symmetry breaking perturbation of the same magnitude. On the other hand, the perturbed states are insusceptible to the identical perturbation that produced them. Although we can define stability for the unperturbed

states by the absence of instability towards any symmetry breaking perturbation, we are confronted with the need to specify exactly the perturbation against which the perturbed state is unstable. The reason is that there is exactly one type of perturbation that restores symmetry, whereas there are many more that break symmetry originally. Therefore, though tempting, we cannot call a perturbed state stable when the unperturbed state becomes unstable in the same above defined sense. What is the proper way to define stability for quantum states? The following change in the point of view promises a solution: Instead of successively perturbing a particular state several times, we look for the ensemble of perturbations that generates the same individual results when directly applied to the unperturbed state. Thus we neglect the history of a particular perturbed state and obtain an ensemble of directly perturbed states that does not change under further perturbation.

In this paper, we propose a solution to the three problems by proceeding as follows: Beginning with a brief introduction to the eigenvalue problem of the Darling–Dennison Hamiltonian for triatomic  $AB_2$  molecules of symmetry  $C_{2v}$ , we formally develop a stability criterion for the normal to local character transition in those molecules on the basis of random matrix theory. According to the discussion above, it seems cumbersome to define stability of a single state in terms of an individual response to a specific perturbation of given magnitude. In contrast, we define stability of an ensemble of eigenstates in terms of the statistics of its response to an ensemble of random perturbations of given magnitude. Then we carry out the stability analysis explicitly for triatomic molecules  $AB_2$  of symmetry  $C_{2v}$  and show that, in particular for the water molecule, the individual response to the most effective specific perturbation almost coincides with the most probable response to an ensemble of random perturbations for the same magnitude of perturbation. For more complex molecules, this suggests the use of an ensemble of random perturbations in order to find a very effective perturbation for detecting susceptible states. On the basis of the analytical and numerical results presented in this and previous studies,<sup>6,14</sup> we propose a generalization of the local stability criterion to other classes of symmetric and nonsymmetric molecules. Stability properties are assigned to the ensemble of perturbed eigenstates that is invariant under an ensemble of random perturbations. Finally, experiments in the low density gas phase, high density gas phase, and condensed phase are suggested.

## II. THE EIGENVALUE PROBLEM OF THE DARLING–DENNISON HAMILTONIAN

The quantum mechanical Darling–Dennison Hamiltonian for two coupled stretch vibrations in its local form may be written, omitting couplings of higher order than (1:1)<sup>9</sup>

$$\hat{H}_{\text{DD}} = (\omega + \xi \hat{I}) \hat{I} + \hat{C}, \quad (1)$$

$$\hat{C} = \hat{\zeta} \hat{I}_x + \chi \hat{I}_z^2, \quad (2)$$

where

$$\hat{I}_x = \hat{a}_1^\dagger \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_1, \quad (3)$$

$$\hat{I}_y = -i(\hat{a}_1^\dagger \hat{a}_2 - \hat{a}_2^\dagger \hat{a}_1), \quad (4)$$

$$\hat{I}_z = \hat{n}_1 - \hat{n}_2, \quad (5)$$

$$\hat{I} = \hat{n} + 1, \quad (6)$$

$$\hat{\zeta} = \frac{1}{2}[\beta + \frac{1}{2}\eta(\hat{n} + 1)], \quad (7)$$

and

$$\xi = \frac{\alpha + \alpha_{12}}{4}, \quad (8)$$

$$\chi = \frac{\alpha - \alpha_{12}}{4}. \quad (9)$$

Here  $\hat{a}_i^\dagger$  and  $\hat{a}_i$ ,  $i = 1$  and  $2$ , are raising and lowering operators defined by their action on the state of the  $i$ th local anharmonic oscillator

$$\hat{a}_i |n_i\rangle = \sqrt{n_i} |n_i - 1\rangle, \quad (10)$$

$$\hat{a}_i^\dagger |n_i\rangle = \sqrt{n_i + 1} |n_i + 1\rangle. \quad (11)$$

The number operator  $\hat{n}_i$  and total number operator  $\hat{n}$  are given by

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i, \quad (12)$$

$$\hat{n} = \hat{n}_1 + \hat{n}_2. \quad (13)$$

The Hamiltonian parameters  $\omega$ ,  $\alpha$ ,  $\alpha_{12}$ ,  $\beta$ , and  $\eta$  are obtained by modeling the observed spectrum and can be interpreted in terms of the physical picture of two identical harmonically coupled Morse oscillators where  $\omega$  is the fundamental frequency of the oscillators,  $\alpha$  is the anharmonicity constant, and  $\alpha_{12}$  is the cross anharmonicity constant. Note that the proportionality factor  $\hat{\zeta}$  associated with the harmonic coupling  $\hat{I}_x$  increases linearly with the total number of vibrational quanta, which indicates that the coupling between the two oscillators for the  $n$ th excited state exceeds by a fraction of  $\eta n/4$  of the ground state value  $(\beta + \eta/2)/2$ .

Let us denote the eigenstates of  $\hat{I}$  by  $|\phi_I, l\rangle = |n-l\rangle|l\rangle$ ,  $\langle \phi_I, l | \phi_I, k \rangle = \delta_{lk}$ ;  $l, k = 0, 1, \dots, n$ ; and the symmetrized eigenstates of  $\hat{I}$  by  $|\phi_I, l, \pm\rangle$ . In the  $|\phi_I, l, \pm\rangle$  local mode representation,  $\mathbf{H}_{\text{DD}}$  decomposes into symmetric tridiagonal blocks  $\mathbf{H}_{\text{DD}}^{l, \pm}$  with eigenstates  $|\Psi_I, \pm, L\rangle$  and eigenvalues  $E_I^{l, \pm}$ ,  $L = 0, 1, \dots$ , with  $L$  a counting index. In the limit  $\zeta \rightarrow 0$ , the eigenstates appear as doubly degenerate states  $|\phi_I, l\rangle$  and in the limit  $\chi \rightarrow 0$ , they appear as nondegenerate states  $|\phi_I, l, \pm\rangle$ .

## III. STABILITY OF EIGENSTATES UNDER RANDOM PERTURBATIONS

In the following, we will investigate the stability properties of eigenstates of  $\hat{H}_{\text{DD}}$ .

In order to facilitate a later comparison between the response to the most effective perturbation and the most probable response to an ensemble of random perturbations, let us briefly recapitulate<sup>14</sup> the construction of the most effective perturbation. As we will demonstrate, this most effective perturbation is generated by an energy mismatch between the

two local oscillators. The question of stability can be put onto a quantitative scale by determining the magnitude of that specific symmetry breaking perturbation necessary to cause localization to a specified extent. Eigenstates of local character become unstable against localization to a specified extent at smaller magnitudes of a symmetry breaking perturbation than occurs for eigenstates of normal character.

The perturbed Hamiltonian, including an energy mismatch of magnitude  $2\epsilon$ , is given in the form

$$\hat{H}_{\text{DD,P}} = \hat{H}_{\text{DD}} + \epsilon \hat{I}_z. \quad (14)$$

The eigenstates of  $\hat{H}_{\text{DD,P}}$  are denoted by  $|\Psi_{I,\pm,L}\rangle_P$ . In the basis of eigenstates  $|\Psi_{I,\pm,L}\rangle$  of  $\hat{H}_{\text{DD}}$ , the perturbation is diagonal in blocks of size  $I$  which we denote by  $\mathbf{I}_{z,I}$ . The induced difference between vibrational excitations of the two local oscillators is given by the expectation value of the **order parameter**  $\hat{I}_z$  for the *perturbed state*  $|\Psi_{I,\pm,L}\rangle_P$ , denoted by

$$I_{z,I,\pm,L}(\epsilon) = \langle \hat{I}_z \rangle_P. \quad (15)$$

The **susceptibility** of the unperturbed eigenstates  $|\Psi_{I,\pm,L}\rangle$  to the symmetry breaking perturbation  $\hat{I}_z$  is defined by

$$\gamma_{I,\pm,L} = \left[ \frac{\partial I_{z,I,\pm,L}(\epsilon)}{\partial \epsilon} \right]_{\epsilon=0}. \quad (16)$$

In general, the susceptibilities and order parameters are easily accessible by numerical calculation. For a detailed discussion, see Ref. 14.

We now turn to the construction of the stability criterion for an ensemble of eigenstates to  $\hat{H}_{\text{DD}}$  under an ensemble of random perturbations. Instead of the perturbation  $\hat{I}_z$ , we now impose an arbitrary perturbation to  $\hat{H}_{\text{DD}}$  in the form of a random operator  $\hat{G}$ , which is an element of an ensemble of random operators to be determined in the following: In analogy to Eq. (14), we write for the perturbed Darling–Dennison Hamiltonian

$$\hat{H}_{\text{DD,P}} = \hat{H}_{\text{DD}} + \epsilon \hat{G}. \quad (17)$$

Let us choose as a basis for the representation of  $\hat{G}$  the basis of eigenstates  $|\Psi_{I,\pm,L}\rangle$  of the unperturbed Hamiltonian  $\hat{H}_{\text{DD}}$ . This defines the square random matrix  $\mathbf{G} = \{ \langle \Psi_{I',\pm',L'} | \hat{G} | \Psi_{I,\pm,L} \rangle \}$ . Let us assume the matrix elements of  $\mathbf{G}$  to be independent identically distributed random variables subject to certain additional restrictions. These restrictions may arise from conservation laws or symmetry requirements.

The specific perturbation  $\hat{I}_z$  is contained in the ensemble of random operators  $\hat{G}$ . Since we want to use the same magnitude  $\epsilon$  for both the most effective and any other random perturbation, let us normalize  $\mathbf{G}$  such that the largest matrix element is of magnitude  $I-1$  which equals the magnitude of the largest matrix element in  $\mathbf{I}_{z,I}$ .

We are interested in the case of intermediate  $I$  and small  $\epsilon \ll \zeta$ , i.e., small perturbations at intermediate levels of excitation. In this region of parameters, we do not expect significant changes in the spectrum due to  $\mathbf{G}$ . However, we do expect significant changes in the locality properties of the eigenstates. Let us impose the following additional restrictions on the ensemble of random matrices  $\mathbf{G}$ . First, let us

make the approximation that  $I$  is conserved, i.e., due to the large energy differences between different polyads for intermediate  $I$ , only states within the same polyad are mixed appreciably by the weak perturbation. Therefore we may assume  $\mathbf{G}$  to be diagonal in blocks  $\mathbf{G}_I$  of size  $I$ . Second, let us impose the condition that the statistical properties of  $\mathbf{G}_I$  are invariant under the similarity transformation that diagonalizes  $\mathbf{H}_{\text{DD}}^I$ . Since the blocks  $\mathbf{H}_{\text{DD}}^I$  are real symmetric matrices, the transformation in question must be orthogonal. Therefore the ensemble of random matrices  $\mathbf{G}$  is given by the Gaussian orthogonal ensemble (GOE) known from nuclear physics.<sup>15</sup>

Let us recapitulate the properties of  $\mathbf{G} \in \text{GOE}$  so far. The matrix representation consists of real symmetric blocks of size  $I$  with independent Gaussian distributed matrix elements normalized such that the largest entry is of magnitude  $I-1$ ; they are similar under orthogonal transformations.

Note that the symmetry properties of a particular molecular system or physical process may cause these restrictions to be modified and that neither the perturbation  $\hat{I}_z$  nor any single other member of the GOE is necessarily invariant under the orthogonal transformation that diagonalizes  $\hat{H}_{\text{DD}}$ .

Furthermore let us retain the definitions for the order parameter in Eq. (15) and for the susceptibility in Eq. (16) for the GOE perturbations. We are interested in reasonably small  $\epsilon \ll \zeta$ . For this region, only the eigenstates  $|\Psi_{I,\pm,L}\rangle_P$  can be completely localized to give  $|I_{z,I,\pm,L}| = I-1$ , and the others only to a certain fraction of  $I-1$ .<sup>14</sup> Therefore we define the relative degree of locality  $\Lambda_{I,\pm,L}$  of a state  $|\Psi_{I,\pm,L}\rangle_P$  by

$$\Lambda_{I,\pm,L} = \frac{|I_{z,I,\pm,L}|}{I - (2L+1)}, \quad 1 \geq \Lambda_{I,\pm,L} \geq 0, \quad (18)$$

which takes the value  $\Lambda_{I,\pm,L} = 1$  for maximum possible localization and  $\Lambda_{I,\pm,L} = 0$  for maximum possible delocalization.

Now we can define a statistical measure of the relative degree of locality under an ensemble of random perturbations of given magnitude as follows:

Let  $P_{\epsilon,I,\pm,L}(\Lambda | u \geq \Lambda \geq l)$  be the probability that, given a GOE perturbation of magnitude  $\epsilon$ , the eigenstate  $|\Psi_{I,\pm,L}\rangle_P$  to  $\hat{H}_{\text{DD,P}}$  has an relative degree of locality  $\Lambda_{I,\pm,L}$  between the lower limit  $\Lambda_{I,\pm,L} = l$  and the upper limit  $\Lambda_{I,\pm,L} = u$ ,  $l \geq u \geq 0$ .

The density function  $P_{\epsilon,I,\pm,L}(\Lambda | u \geq \Lambda \geq l)$  is accessible through a simple numerical scheme. In this way, we propose a local **stability criterion** for the transition from states of normal character to states of local character.

At given  $\epsilon$ , an ensemble of eigenstates  $|\Psi_{I,\pm,L}\rangle_P$  is stable local if  $P_{\epsilon,I,\pm,L}(\Lambda | I \geq \Lambda > 0.5) > 0.5$ , stable normal if  $P_{\epsilon,I,\pm,L}(\Lambda | I \geq \Lambda > 0.5) < 0.5$ , and neutrally stable if  $P_{\epsilon,I,\pm,L}(\Lambda^{\text{rel}} | I \geq \Lambda > 0.5) = 0.5$ . A point of bifurcation for an eigenstate is given by the value of  $\epsilon$  for which a change in stability occurs.

## IV. DISCUSSION

The construction given above appears to be rather technical. In the following, we comment on it and explore its physical content.

According to the Introductory section, the origin and action of the random operator  $\hat{G}$  that perturbs the Hamiltonian  $\hat{H}_{\text{DD}}$  can be justified and interpreted in many ways.

For small  $(I, \epsilon)$ ,  $\hat{G}$  may reflect scattering processes between states mediated by weak coupling of the molecule to an inhomogeneous environment, i.e., the energy flow from one degree of freedom in the molecule to another does not take place within the molecule, but through a channel in the environment. If the environment is inhomogeneous, these channels may appear at random and thus lead to the random matrix elements in the molecular Hamiltonian.

For large  $(I, \epsilon)$ , the interaction between states of the isolated molecule may be so complex that the eigenvalues of  $\hat{G}$  describe the spectrum to good approximation. That region is commonly referred to as the chaotic region of the spectrum. Note that the field that induces population of the highly excited states may cause inhomogeneities that deserve consideration.

Similarly,  $\hat{G}$  may also account in some way for the uncertainty in the Hamiltonian parameters that are obtained from fits to experimental spectra owing to perturbations by coupling mechanisms not explicitly included. From this point of view, it seems reasonable to check the stability of any eigenstate calculation based on approximate algebraic Hamiltonians and mandatory to check the stability of a wave packet propagation for highly excited states.

The resulting ensemble of Hamiltonians  $\hat{H}_{\text{DD},P}$  generates for each given  $\epsilon$  an ensemble of eigenstates  $|\Psi_I, \pm, L\rangle_P$  that is invariant under GOE perturbations. Therefore it is possible to assign to that ensemble of states properties that do not require further specification of the applied perturbation. A property of interest for the normal to local character transition in  $AB_2$  molecules with  $C_{2v}$  symmetry is the degree of locality of a vibrational excitation defined by Eq. (18). The distribution of the degree of locality over the ensemble of perturbed states is obtained by equally weighting the response to each single  $\hat{G}$ . If more than half of the ensemble of perturbed eigenstates show localization of vibrational excitation to more than half of the possible degree, it is reasonable to call that ensemble stable local. Whereas for the classical correspondent we are certain that the local modes become stable when the normal modes become unstable, for the underlying quantum system at that particular magnitude of perturbation, we expect only that a particular state be more localized than delocalized. Note that probabilistic concepts enter the picture in two ways. First, via the probabilistic interpretation of the quantum mechanical expectation value, and second, via the expectation value over the response to an ensemble of random perturbations under some probability weight which we chose to be the same for all responses.

Let us establish by example the connection between the effects of the supposedly most effective perturbation  $\hat{I}_z$  and the random perturbations  $\hat{G}$  on the eigenstates of  $\hat{H}_{\text{DD}}$ . The calculation of the order parameter diagram for perturbation by  $\hat{I}_z$  is straightforward.<sup>14</sup> For GOE perturbations, we implemented the following numerical scheme for  $\text{H}_2\text{O}$ :  $I=10$ ,  $-12 \leq \log(\epsilon) \leq 4$  to obtain the density function  $P_{\epsilon,10,\pm,L}$ . The logarithmic scale of  $\epsilon$  is divided in 49 equal parts and the order parameter evaluated at each of the 50 points for  $10^4$

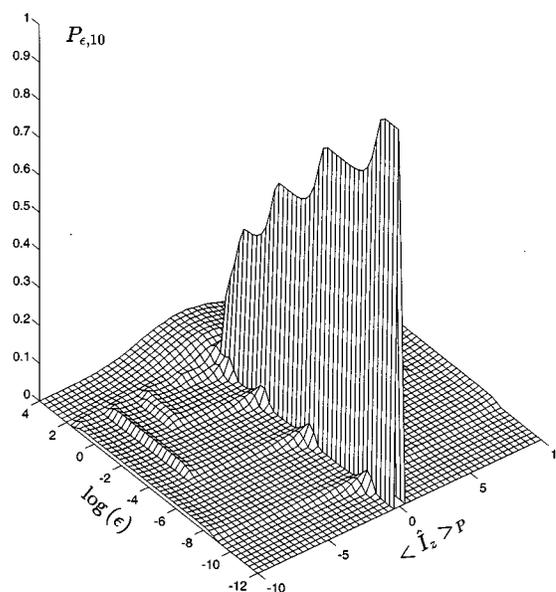


FIG. 1. Probability distribution  $P_{\epsilon,10}$  for  $\text{H}_2\text{O}$ . The  $\langle \hat{I}_z \rangle_P$  axis indicates the order parameter, i.e., the difference in the number of vibrational quanta localized in the bond oscillators. The  $\log(\epsilon)$  axis indicates the decadic logarithm of the strength of the random perturbation in units of wave numbers. The  $P_{\epsilon,10}$  axis indicates the probability that for a given strength of perturbation  $\epsilon$ , an eigenstate  $|\Psi, \pm, L\rangle_P$  has an associated order parameter of the value  $\langle \hat{I}_z \rangle$ . Large magnitudes of the order parameter indicate significant localization of vibrational excitation. If significant localization occurs at small strengths of perturbation, the associated eigenstate is not robust. For further explanation, see Sec. IV.

successively generated random perturbations  $\mathbf{G}_{10} \in \text{GOE}$ . The range of the order parameter  $|I_{z,10,\pm,L}| \leq 9$  is divided into 51 equal intervals and the number of calculated order parameters within each interval counted. The probabilities are obtained by normalization of those counts by the total number of counts for given  $\epsilon$ . Using counting statistics as a rule of thumb, we estimate the accuracy of the probabilities to be  $1/\sqrt{10^4} = 0.01$ . For the purpose of compact representation, the results  $P_{\epsilon,10,\pm,L}$  were combined into the distribution  $P_{\epsilon,10}$  for all eigenstates  $I=10$  and further normalized to one. The result is shown in Fig. 1.

Let us briefly summarize the main features. First of all, we notice for small  $\epsilon$  the dominant peak in  $P_{\epsilon,10}$  around  $I_{z,10,\pm,L}=0$ . This peak represents all counts of states for which  $I_{z,10,\pm,L} \leq 0.18$ . Its value decreases from 1 for the unperturbed ensemble in discrete steps of approximately 0.2. This corresponds to successive pairs of eigenstates  $|\Psi_{10,0,\pm,0}\rangle_P, |\Psi_{10,0,\pm,1}\rangle_P, |\Psi_{10,0,\pm,2}\rangle_P, \dots$  becoming localized to more than 2% of the absolute possible value  $I_{z,10,\pm,L}=9$ . Second, we see that at  $\Lambda_{10,\pm,L} \approx 1$ , for each state, maxima in  $P_{\epsilon,10}$  develop. After a cascade of four decreases in the center peak, the dominant peak and the outer maxima disappear and a broad distribution with a single maximum at  $I_{z,10,\pm,L}=0$  forms. For each state, the contour line of maximal height has a sigmoid shape and indicates the single most probable response to a random perturbation. This can be more clearly seen from the contour plot in Fig. 2. Over a certain region of  $\epsilon$  the single most probable response changes from almost no locality to almost total locality, i.e.,

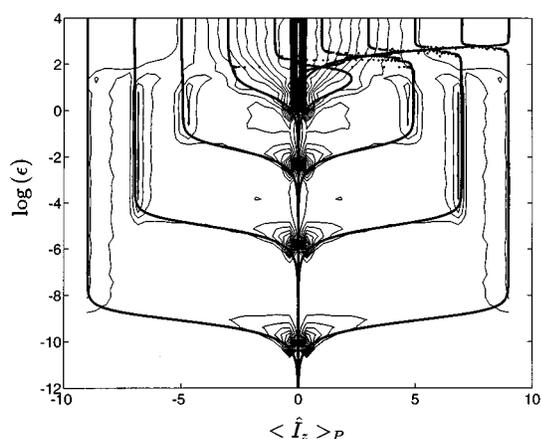


FIG. 2. A contour of probability distribution  $P_{\epsilon,10}$  for  $\text{H}_2\text{O}$  (indicated as thin lines) under random perturbations, superimposed by the order parameters under the most effective  $\hat{I}_z$  perturbation (indicated as a thick line). The most probable response under randomly picked perturbations coincides with the response to the most effective perturbation. For further explanation, see Sec. IV.

a qualitative change in the stability properties occurs. The notion of a bifurcation point has been attached to the value of  $\epsilon_{\text{bif}}$ , where the expectation of locality is larger than one-half.

Figure 2 shows the contour plot of  $P_{\epsilon,10}$  on which is superimposed the order parameter plot for the  $\hat{I}_z$  perturbation. We see that the contours of maximal height almost coincide with the order parameter for the systematic perturbation after the bifurcation. From the graph, we see that the bifurcation point coincides in good approximation with the point of inflection of the sigmoid given by the top contour. Since the most probable single response lags behind the response to that particular single systematic perturbation, it is reasonable to call this perturbation more effective than the average perturbation. Since it causes the maximum possible localization at larger values of  $\epsilon$ , we may call it the most effective perturbation.

The surprising aspect is that the most probable response and the largest possible response are so close. The reason can be outlined as follows: Consider the projection of any GOE perturbation onto the  $\hat{I}_z$  perturbation. Let us assume for the sake of argument that the magnitude  $\theta$  of the projection is uniformly distributed between 0 and 1, i.e.,  $\epsilon \hat{G} = \epsilon \theta \hat{I}_z + \epsilon(1-\theta) \hat{G}'$ ,  $0 \leq \theta \leq 1$ . Thus for any random perturbation for which  $\epsilon \theta > \epsilon_{\text{bif}}$ , we expect the maximum possible response. Under equidistribution of projections for values of  $\epsilon \gg \epsilon_{\text{bif}}$ , this will be most probable, i.e., almost any perturbation will be most effective.

This connection between the  $\hat{I}_z$  perturbation and other GOE perturbations is vital from a practical point of view. For the  $\hat{I}_z$  perturbation we can analytically predict for which range of Hamiltonian parameters and degree of excitation the molecular system will become unstable. In addition, as we have pointed out in a previous investigation,<sup>14</sup> we can obtain the bifurcation points for individual states in good approximation by evaluation of the order parameter associated with Eq. (14) and in reasonable approximation from the inverse of

the susceptibilities. This is the reason why we chose the stability criterion in its particular form.

Therefore we can analytically predict the onset of instability of a vibrational excitation in the molecular system and of each individual state under an ensemble of randomly occurring perturbations.

The straightforward application of the normal to local character stability criterion to the water molecule shows that at a GOE perturbation  $\epsilon \approx (10^{-7} \text{ cm}^{-1})$ , the eigenstates  $|\Psi_{10, \pm, 0}\rangle$  become unstable normal and the corresponding perturbed eigenstates  $|\Psi_{10, \pm, 0}\rangle_P$  become stable local. This coincides with the prediction from the analytical results  $\tilde{\kappa}(I=10) < 1$  and  $n^2/\gamma_{10, \pm, \sigma} \approx O(10^{-7} \text{ cm}^{-1})$ .<sup>14</sup>

To finish the discussion, let us briefly return to the example of molecules in an inhomogeneous solid matrix and show how to implement the outlined procedure. Consider water molecules embedded in an inhomogeneous solid matrix that are prepared in one of the vibrational states  $I=10$ . The solid will be at room temperature and the coupling  $\epsilon$  of solid matrix and molecules will be weak, say of  $O(\text{cm}^{-1})$ . We are interested whether the dipole moment of the water molecules is very robust under these conditions, i.e., comparable to the low density gas phase molecules at the same  $I$ , for which it is reasonable to assume  $\epsilon \rightarrow 0$ . Instead of considering each single molecule and the influence of its particular environment, we may consider the effect of the single most symmetry breaking environment that perturbs the molecule with comparable strength. That is, we calculate the most probable response of the dipole moment from the response to the most effective perturbation at given  $\epsilon$ . Furthermore, let us assume that a local distortion with energy  $D$  increases the strength of the coupling between molecule and environment from  $\epsilon$  to approximately  $\epsilon_T(D) \approx \epsilon + (\partial\epsilon/\partial D)_T D$ , i.e., we have to consider the various possible  $\{\epsilon_T(D)\}$  at the temperature  $T$ . Thus we have to weigh each most probable response for given  $\epsilon_T(D)$  by the Boltzmann factor  $\exp(-D/kT)$  at room temperature. If we assume  $(\partial\epsilon/\partial D)_T = O(10^{-1} \text{ cm}^{-1})$  then  $\epsilon_T(D) > O(10 \text{ cm}^{-1})$  become rather unlikely.

From Fig. 2, we see that at perturbations  $\epsilon \gg O(\text{cm}^{-1})$ , the four lowest lying states are stable local, i.e., we may use the localized eigenstates to compute the dipole moment. The dipole moment for those molecular states in the solid matrix is certainly increased compared to the equivalent molecular states in the gas phase. We conclude that under this change of external conditions, the dipole moment of the four lowest lying states is not robust. For the following four states, the Boltzmann weighting at room temperature becomes important, since it spreads  $\epsilon$  over the bifurcation points. Thus it is necessary to choose an ensemble of eigenstates to calculate the dipole moment and to decide over its robustness. Finally, since  $\epsilon_T(D) > O(10 \text{ cm}^{-1})$  is rather unlikely at room temperature, we expect the dipole moment of the two highest lying states to be fairly robust, i.e., the same for the molecular states of the low density gas phase and the molecular states of the inhomogeneous solid matrix at  $I=10$ .

## V. CONCLUSION

The question of robustness of physical properties of molecules leads directly to the issue of the stability of eigen-

states under perturbations. Instability can occur for various degrees of freedom, e.g., rotational, vibrational, and electronic degrees of freedom. To be explicit, we developed the theory for vibrational eigenstates, i.e., in the framework of the normal to local mode transition in polyatomic molecules where from earlier treatments some open question remained. In conclusion, let us summarize the answers to the questions posed initially and generalize the results.

First, the choice of a specific symmetry breaking perturbation to probe the instability against any symmetry breaking perturbation can be justified from the observation that the response to the *most effective* symmetry breaking perturbation almost coincides with the *most probable* response under an ensemble of random perturbations. Thus this response under the most effective perturbation is representative for the behavior under any perturbation.

Conversely, for complex symmetric molecules, the instability against symmetry breaking perturbations can be investigated taking almost any random perturbation. Such a perturbation is easily found since the most probable response appears to be close to the maximum possible response.

Third, the statistics of the response of an ensemble of eigenstates to an ensemble of random perturbations of given magnitude defines their stability. The entire ensemble or a fraction of it is considered stable if in response to the perturbation at most half of the ensemble within previously specified limits is shifted outside those limits. The response can be described most simply by the overlap of the unperturbed and perturbed eigenstates or more sensible measures like order parameters that indicate reduction in symmetry. The ensemble of random perturbations can be chosen in a variety of ways. In the simplest case, the proper random ensemble is chosen according to the transformation that diagonalizes the Hamiltonian and applied without further restrictions. By imposing restrictions such as conservation laws or symmetry requirements, the perturbation can become of increasing selectivity in the sense that only a certain fraction of states will respond.

For the class of  $AB_2$  molecules with  $C_{2v}$  symmetry, these conclusions are based on analytical arguments that allow us to predict the onset of instability of vibrational excitations and the extent of instability for each individual state in terms of the Hamiltonian parameters and the degree of excitation.

We emphasize that the magnitudes of perturbation necessary to cause localization are extremely small compared to typical magnitudes of couplings between local oscillators. Therefore almost any small inhomogeneity in the surroundings of a molecule that contains an unstable normal excitation will cause localization of that excitation under reduction of the molecular symmetry.

It is straightforward to apply this procedure to polyatomic molecules of higher symmetry than  $C_{2v}$  or even to molecules without symmetry, where it may reveal a tendency towards localization beyond what must be expected from the mere absence of symmetry. The local to normal character stability criterion is then easily generalized.

At given  $\epsilon$ , an ensemble of eigenstates is stable local if  $P_{\epsilon,\Psi}(\Lambda|I \geq \Lambda > 0.5) > 0.5$ , stable normal if

$P_{\epsilon,\Psi}(\Lambda|I \geq \Lambda > 0.5) < 0.5$  and neutrally stable if  $P_{\epsilon,\Psi}(\Lambda|I \geq \Lambda > 0.5) = 0.5$ . A point of bifurcation for an eigenstate is given by the value of  $\epsilon$  for which a change in stability occurs.

$P_{\epsilon,\Psi}$  contains the statistics of the response of the ensemble of eigenstates  $|\Psi\rangle$  in terms of the random variable  $\Lambda$  that indicates the relative degree of locality of the perturbed eigenstates  $|\Psi\rangle_p$  under the ensemble of random perturbations.  $P_{\epsilon,\Psi}$  and  $\Lambda$  can be defined for each particular case in analogy to the proposals made above. We have thus demonstrated that the notion of robustness can be quantitatively addressed on the basis of the introduced susceptibilities.

Before we draw conclusions for the applicability of the stability criterion in experiments, some final remarks on related theoretical issues are in order. There have been large efforts to illuminate the relevance of instability in classical systems that are correspondents to quantum systems.<sup>16</sup> In the regime of classical chaos, the quantum mechanical Green's function can be approximated by a classical counterpart, sometimes called Gutzwiller's trace,<sup>17</sup> that only includes contributions from classical periodic orbits. There is no apparent connection of the stability of those classical orbits and the stability of the eigenstates as discussed in this paper. However, as discussed in an earlier paper,<sup>14</sup> there is a connection between a classical bifurcation and the appearance of eigenstates of high susceptibility. The topic is still under investigation.

The stability criterion is relevant for the following experiments:

First, we want to point out the connection of this work to the problem of optimum control of intramolecular dynamics by laser fields.<sup>18</sup> The inherent uncertainty about the exact form of the Hamiltonian and experimental errors are both modeled by the GOE. Therefore the language of susceptibilities may be very useful in the context of the stability issue of optimum control schemes.

Collision induced energy transfer is another area in which we expect the differing susceptibilities of vibrational eigenstates to be important. In Oka's definitive treatment of propensity rules,<sup>19</sup> the preferred collision induced transitions are derived from the symmetry properties of the permanent multipole moments of the molecule in its equilibrium configuration. These propensity rules work quite well, especially in systems where at least one of the collision partners has a permanent low-order multipole. In some other systems, dominated by short range collisions, these propensity rules do not correctly predict the most rapid rates. Recent experimental results on rotational energy transfer in methane<sup>20</sup> have found a propensity to conserve parity in spite of the fact that parity change is expected because the octopole moment is the lowest order permanent moment in methane. Lowering of the molecular symmetry during hard collisions, resulting in a quadrupole moment, is one possible explanation. Our results suggest that the breakdown of propensity rules based on the lowest order permanent moment would be most evident for vibrational states in a polyad that have the largest susceptibilities. This prediction is now open to experimental test with techniques like those of Ref. 20.

In still another area, collision-induced spectra are spectra

which occur at high pressure because of absorption during the symmetry breaking collision process. These intensities are quadratic in the number density. Our results lead us to suggest that collision-induced spectra would appear first for vibrational states with high susceptibilities, for instance, parity forbidden  $g-g$  transitions in acetylene.

## ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and the Air Force Office of Scientific Research (AFUSR-F4962U-94-1-0068).

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