Structure, dynamics and spectroscopy of single molecules: A challenge to quantum mechanics

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Spectroscopy of an *ensemble* of molecules gives information about (differences of) eigenvalues of the molecular Hamiltonian and "transition probabilities". All this information is encoded in the thermal non-pure state with density operator D_β. No information is offered on the *pure* states of the actual *individual* molecules. In response theory, for example, a spectroscopic experiment is described by an input-output equation which depends only on the thermal density operator D_β and *not on a particular decomposition of D_β into pure states*.

Spectroscopy of *single* molecules gives more information than just (differences of) eigenvalues of the molecular Hamiltonian and transition probabilities. One has, for example, an additional stochastic ("migrating") behaviour of lines, which is not reconcilable with response theory. Also, the derivation of dissipative single-molecule behaviour cannot be done by usual response theory, since expectation values (of the output observable) with respect to a pure state cannot be measured without perturbing this pure state itself. Only *averaging* over the stochastic behaviour of many molecules results in the regular dynamics used in response theory.

Here "single-molecule spectroscopy" is always meant to refer to the quantum joint system {single molecule & environment}, where the environment can, for example, consist of the matrix in which the single molecule is embedded or the quantum radiation field. The question *"What is the influence of the molecular environment?"* will be an important background for the discussions in this paper, even when it is not explicitly mentioned and discussed. Hence all the questions posed below refer to "isolated" single molecules as well as to the joint system {molecule & environment}, even when they are only formulated for isolated single molecules.

Single molecule-spectroscopy should finally give answers to questions like the following, always referring to pure states of individual molecules and *not* to the thermal non- pure state D_β:

- Superpositions of left- and right-handed states of a chiral molecule seem to be unstable under small external perturbations. What is the time necessary to decay into either a left- or a right-handed state? What is the stochastic dynamics for such a decay?
- Similarly, superpositions of states of different molecular isomers (having the same Hamiltonian and the same thermal state) seem to be unstable under external perturbations. Or superpositions of states of a magnet having positive and negative permanent magnetization seem to be unstable under external perturbations. What is the transition time between such unstable superpositions and stable states? The latter are usually not eigenstates of the molecular Hamiltonian in question.

• Which is the observable measured in a single-molecule spectroscopic experiment? The Hamiltonian or the dipole moment operator? Does an arbitrary initial state become an eigenstate of the molecular Hamiltonian (Bohr's point of view) or an eigenstate of the dipole moment operator (von Neumann's point of view)?

To look at these and other questions theoretically, decompositions of the thermal state D_β into pure states must be investigated. Any decomposition of D_β into pure states preserves the statistical results but gives a model for *single*-molecule spectroscopic behaviour. There are uncountably many different possibilities to decompose a non-pure state like D_β into pure states. Here the decomposition of the thermal state into *eigenstates of the molecular Hamiltonian* is not generally accepted, because eigenstates are, in many circumstances, unstable under small perturbations.

For a decomposition of the thermal state D_β into pure states it is neither compulsory to use orthogonal nor compulsory to use only countably many pure states (corresponding to a basis of the underlying Hilbert space). In the context of the Born–Oppenheimer approximation, for example, one might try to look for a general (non-orthogonal) decomposition which *minimizes the dispersion of the positions of the nuclei* in the molecule. Here a different approach is presented using *Jaynes' maximum-entropy principle* applied to decompositions of thermal non-pure states into pure states: "Decompose thermal non-pure states into pure states in such a way that the resulting ensemble μ_{max} of pure states has maximal entropy with respect to equipartition of pure states." Here "equipartition of pure states" is *not* equipartition of eigenstates, but equipartition of *all possible* pure states. It is argued that the (uniquely determined) maximum-entropy ensemble μ_{max} describes a *stable* decomposition of D_β under small external perturbations.

With respect to the stable maximum-entropy decomposition, unstable states such as the above-mentioned superpositions appear but with very low probability. A dynamical interpretation of the maximum-entropy principle is proposed. Though, at the present stage, life times of the abovementioned superpositions (or the time necessary for a quantum jump) cannot be computed, a *martingale approach is sketched which allows to compute transition probabilities between arbitrary pure initial and final states* (i.e., not restricted to eigenstates of the Hamiltonian). Incidentally, the choice of a stable decomposition is related to the Born–Oppenheimer approach: certain superpositions are "excluded" by taking "localized" eigenstates (existing in a certain minimum of the BO-potential).

The present approach is checked for the quantum-mechanical Curie-Weiss model of a magnet. The question there is how "fast" the specific magnetization gets a classical observable *with increasing number of spins*; how "fast" the superpositions of states with opposite permanent magnetization "die out" with increasing number of spins. Heuristically, one may expect that a magnet consisting of 4 spins does show quantum behaviour, whereas a magnet consisting of 1000 spins already shows a partially classical behaviour. Hence the probability density to find a particular expectation value of the specific magnetization operator $\hat{m}$ may be expected to *concentrate more and more at* the two values $\pm m_\beta$ for positive and negative permanent magnetization (if the temperature is below the Curie point). This is indeed true, and it is shown that this concentration process can be described by an entropy in the sense of fluctuation theory in statistical mechanics (i.e., large- deviations theory). Similarly to this magnetic example, it would be interesting to know how "fast" certain superpositions (e.g., of handed states) disappear in a sequence of molecular species like {monodeuteroaniline → NHDT → naphthazarin → ⋯ → aspartic acid} with decreasing level splitting between the ground and first excited state. It is argued that usual statistical (algebraic) quantum mechanics cannot describe this "soft phase transition", because it imposes too excessive conditions on symmetry breaking and classical structures (arising only in the limit of infinitely many degrees of freedom).

The general idea is the following: It is tried to extract information about individual molecular

behaviour from the statistical information encoded in the thermal state D_β (via the stable maximal entropy decomposition of D_β). The resulting theory on the level of individual pure states is stochastic and nonlinear and can be taken as a starting point to interpret single-molecule spectroscopy from a *quantum-mechanical* point of view. In this theory, quantum jumps are replaced by a continuous dynamics in the space of *all* molecular pure states and the projection postulate is "derived". Correspondingly, on the experimental side, single-molecule spectroscopy gives more (and in particular stochastic) information than encoded in the thermal density operator. The hope is that experimental work in single-molecule spectroscopy will allow to characterize stochastic time-evolutions of single molecules and allow to check the theoretical ideas exposed in this paper.

1. Ammonia-type molecules

The superposition principle is one of the most important concepts of quantum mechanics: Starting from two arbitrary state vectors Ψ_1 and Ψ_2, the wave function

$$c_1\Psi_1 + c_2\Psi_2 \tag{1}$$

is again a legitimate wave function of the system in question. Here c_1 and c_2 are appropriately normalized complex scalars.

Let me try to illustrate the superposition principle using ammonia and ammonia-type molecules. To this end, consider fig. 1: The double-minimum function there is (a sketch of) the Born–Oppenheimer potential for the electronic ground state of ammonia. It is an energy vs. an internal inversion coordinate diagram. Every value of the inversion coordinate corresponds to a particular nuclear frame of ammonia. The two minima, for example, correspond to pyramidal structures, whereas the maximum corresponds to a planar structure. At first sight, ammonia molecules roughly keep their traditional chemical structures even in a quantum description. The pyramidal forms, for example, are described by the rather peaked (non-stationary) wave functions Ψ_L and Ψ_R, and therefore admit at least an approximate nuclear frame. As soon as we consider superpositions of Ψ_L and Ψ_R, things change dramatically. Look at the superposition $\Psi_+ := \frac{1}{\sqrt{2}}(\Psi_L + \Psi_R)$, which describes the proper ground state of ammonia, and at the superposition $\Psi_- := \frac{1}{\sqrt{2}}(\Psi_L - \Psi_R)$, which describes the first excited state of ammonia. Incidentally, the transition between these two states is the ammonia maser transition [1]. With respect to these stationary states, a single ammonia molecule does not have a nuclear frame any more: The nitrogen and hydrogen nuclei do not sit at fixed positions; only probability distributions for their positions can be given, just as is usual with electrons.

Figure 2 is a sketch of the ground state of ammonia. Though still drawn, the

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[1] Actually, if the "handed" states are defined as superpositions of the eigenstates, i.e., the other way round, one could discuss using coefficients 1 and i instead of ± 1.
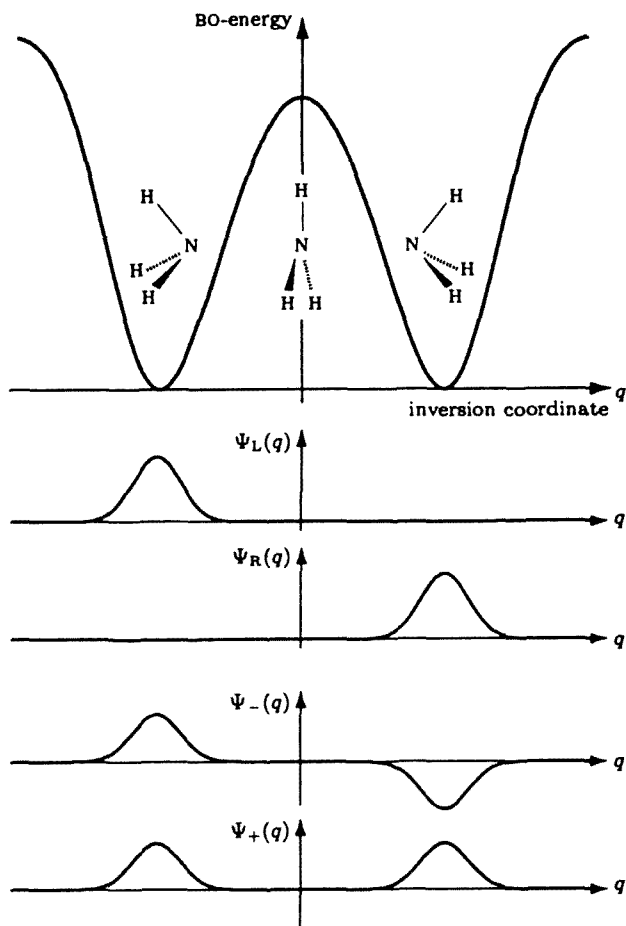
Fig. 1. Illustration of the superposition principle using ammonia and ammonia-type molecules.

nitrogen-hydrogen *bonds* lose their meaning in this context. Hence ammonia does not admit a nuclear frame, at least with respect to the states Ψ_+ and Ψ_-.

Let us now have a look at other molecules of similar type: Monodeuteroaniline [106], naphthazarin and related species [25,32,67,78,89–1,114,115,118,134,135] or properly chiral molecules, such as sulfoxides [65,79], sugars and amino acids. They all have an internal inversion coordinate and the same underlying structure of states, namely two stationary states Ψ_+ and Ψ_-, and nonstationary states Ψ_L and Ψ_R, which are interconverted by a tunneling process (very slow for chiral molecules). In the case of naphthazarin, the inversion coordinate corresponds to a (simultaneous) move of the hydroxylic hydrogen atoms to the respective neighbouring carbonyl groups.

Though for all these different molecular species one can formally write down the wave vectors Ψ_+, Ψ_-, Ψ_L and Ψ_R, their particular situation differs dramatically:
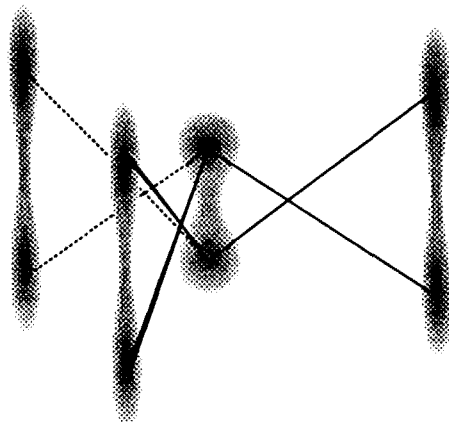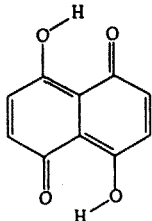
Fig. 2. Sketched distribution of the nuclei in the ground state of an ammonia-type molecule.

For properly chiral molecules (in the sense of traditional chemistry) the states Ψ_+ and Ψ_- have never been observed experimentally; only handed states *seem* [40,41,104,105] to exist. For naphthazarin the situation is not entirely clear (to me, at least), whereas for monodeuteroaniline and ammonia all four mentioned states are accessible experimentally [75].

The main difference between the mentioned molecular species is the different level splitting (i.e., the energy difference $(E_- - E_+)$ between excited and ground state, see table 1). And indeed, heuristic use of quantum-mechanical perturbation theory [112] tells us that "something dramatic" might happen when the level splitting is sufficiently small. It would be quite interesting to have a whole *series of different ammonia-type molecules* interpolating between ammonia and chiral molecules. For the species in such a series the questions would then be:

Table 1
Ammonia-type molecules.

	Barrier	Level splitting
Monodeuteroaniline [106]	5.5 kJ mol^{-1}	600 J mol^{-1}
Ammonia	23.9 kJ mol^{-1}	9.5 J mol^{-1}
Naphthazarin [134]		
	≈ 50 kJ mol^{-1}	≈ 0.02 J mol^{-1}
Aspartic acid	≈ 140 kJ mol^{-1}	$\approx 10^{-60}$ J mol^{-1}

- Does the spectrum show the "maser transition"? [2]

- Can the proper (stationary) ground state be prepared experimentally [40,41,104,105,109]?

- Assuming that the proper (stationary) ground state exists: is it unstable under small external perturbations and how quickly does it decay into the "handed" (or other) states? Can the wave function of the proper ground state (and other states) be determined experimentally (up to a phase factor) by a protective measurement in the sense of Aharonov, Anandan and Vaidman [1]?

- Is there a kind of phase transition in the series of molecular species {monodeuteroaniline → ⋯ → asparagic acid} in table 1?

- Handed states are *not* eigenstates of the molecular Hamiltonian, i.e., non- stationary. What is the role of eigenstates in spectroscopy?

However the situation may be: there is at least some indication that an approximate classical structure appears when the level splitting decreases. Note that all the mentioned species are *small* molecules. Classical or approximate classical structures are therefore not restricted to macroscopic situations.

Chirality is surely not the only example which can be interpreted as an (approximate) classical structure. Consider, for example, circular DNA molecules with identical monomer sequence, which are differently knotted [125,128]. Can such differently knotted states be superposed? Does there exist a state bearing analogy to the ground state of ammonia? Actually, chemistry abounds with classical structures: The nuclear frame and the isomeric type of a molecule (see section 4), or temperature [132] and chemical potential [85] of a substance are further examples.

Or consider a magnet composed of a large but finite number of spins: Can one prepare a superposition of states with opposite magnetization? How fast would such a stationary state decay into its components? Does a kind of phase transition arise with increasing number of spins? What happens with the spectrum when a classical structure appears?

A note in between: "*Approximate* classical structure" is to say that the superposition principle still holds universally, but certain "forbidden" superpositions (as between differently handed states) are unstable and decay quickly into their components. Hence an approximate classical structure does *not* break the superposition principle. Therefore an approximate classical observable is not strictly equivalent to a superselection rule as in algebraic quantum mechanics [33,34,99,117]. Actually, in algebraic quantum mechanics one uses limits (number of particles → ∞; or mass → ∞, or volume → ∞, or nuclear molecular masses → ∞) in order to get to (strict) classical observables or superselection rules. It is interesting and embarras-

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[2] Many experimental problems come in at that point. The transition can, for example, be dipole-forbidden as with naphthazarin. In this case, related P-, Q- and R- transitions could nevertheless be visible.

sing that the superposition principle holds universally before the limit (i.e., for large but finite number of degrees of freedom, for large but finite volume or mass, or for large but finite nuclear molecular masses), whereas the superposition principle is restricted after the limit. Therefore, in contrast to previous papers of the author [8,11], in the present paper the number of degrees of freedom is always taken to be *finite*, though perhaps large!

2. The decomposition of a non-pure state into pure states is not unique

It has been tacitly assumed in this paper that pure quantum states make sense for an *individual* quantum system [3]. This point of view is suggested by investigations like that of Raggio [110], and more and more accepted [23,28,57,59,60,80,100, 101,133,150]. For chemists, this way of talking about micro- and macrosystems as individual entities is quite acceptable: They usually do not change their interpretation when speaking about small molecules, macromolecules, crystals and the contents of an Erlenmeyer flask.

However, attention should be paid to the fact that most quantum-theoretic results refer to a statistical setting in terms of non-pure states. Since non-pure states cannot be *uniquely* decomposed into pure ones, there is no standard way of reformulating such quantum theoretic results for individual systems (i.e., in terms of pure states).

The nonuniqueness of decompositions is illustrated in a simple case, namely for a thermal non-pure state of a *two-level system* with density operator

$$D_\beta = \frac{e^{-\beta E_+} D_+ + e^{-\beta E_-} D_-}{\text{Tr}(e^{-\beta E_+} D_+ + e^{-\beta E_-} D_-)} \ . \tag{2}$$

Incidentally, thermal states ($\equiv \beta$-KMS states) can be defined as being those states which satisfy a certain stability requirement [33,117] under perturbations and the definition via Boltzmann occupation numbers is taken here only for simplicity. The states of a two-level system correspond to the points of a sphere in three-dimensional space (see appendix 1 and fig. 3). In particular, pure states correspond to points on the surface of the sphere, whereas proper nonpure states (with non-idempotent density operators) correspond to inner points of the sphere. The density operator D_β can, of course, be decomposed into the eigenstates Ψ_+ and Ψ_- (see left part of fig. 3). However, entirely different decompositions into two non- orthogonal states Ψ_1 and Ψ_2 are possible (see middle part of fig. 3). Finally, it is not all compulsory to decompose into *two* states: All possible pure states of the two-level system may take part in a decomposition of D_β

$$D_\beta = \int_{S_2} |\xi_{\vartheta,\phi}\rangle\langle\xi_{\vartheta,\phi}| f(\vartheta,\phi) \frac{\sin\vartheta \, d\vartheta \, d\phi}{4\pi} \ , \tag{3}$$

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[3] Even more: it has been assumed that there is a 1-1-correspondence between pure statistical states, on the one hand, and individual states, on the other.
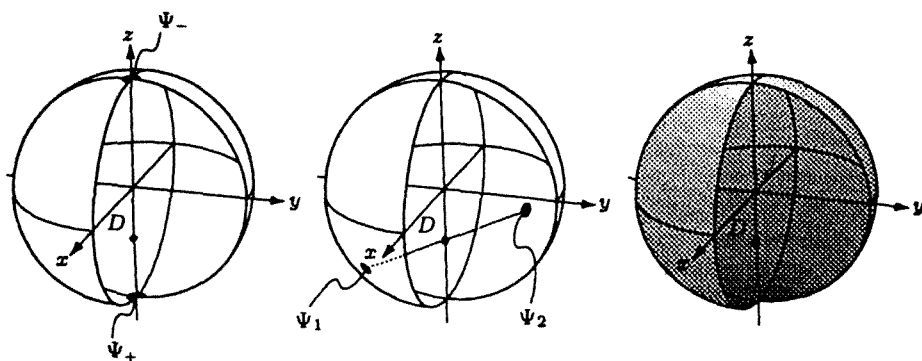
Fig. 3. A non-pure state (with density operator D) can be decomposed in many different ways into pure states. Here the situation is sketched for 2×2- matrices. The left part of the figure shows a decomposition of a density operator D into its eigenstates. The middle part of the figure shows a decomposition of D into two non-orthogonal states. The right-hand part of the figure illustrates the decomposition of D into *all* possible pure states (of a two-level system). The probability density of pure states arising in this decomposition is indicated by the shading.

(using spherical coordinates and Dirac bra-ket notation). Such a decomposition is sketched on the right-hand side of fig. 3, the probability density $f = f(\vartheta, \phi)$ corresponding to the shading in the figure. *Summarizing*: there is a big difference between non-pure states and ensembles of pure states. Any ensemble of pure states gives rise to a unique non-pure state, but not conversely.

Remark

A "mixed" state can have different meanings [17,48]: It can either be a shorthand description of an ensemble of pure states, or arise as restriction of a pure state (e.g., of the joint system {molecule & radiation field}) to a smaller part (e.g., the molecule). In the latter case, it does not necessarily make sense to decompose the "mixed" state into pure states (or only after an appropriate dressing transformation). Here the term "mixed" state is always replaced by *non-pure* state.

3. Deriving Fermi's Golden Rule from statistical quantum mechanics

It is not easy to keep track of the differences between statistical and individual settings of quantum mechanics. As an illustrating example let us consider Fermi's Golden Rule for the transition probabilities between eigenstates of the molecular Hamiltonian. Its derivation to be reviewed here is based entirely on statistical quantum theory in terms of non-pure states (density operators). The keyword in the present context is (linear) *response theory* [54,74,103].

Starting point is some dissipative dynamics as, for example, the Karplus–Schwinger dynamics specified by the differential equation

$$\dot{D}(t) = \frac{1}{i\hbar}[H_0, D(t)] - \Gamma\{D(t) - D_\beta\}, \quad t \geqslant 0, \tag{4}$$

Here the constant Γ determines the dissipation (and finally the line width in the spectrum). The solution $D(t)$ of the Karplus–Schwinger equation converges to the thermal state $D_\beta = \exp(-\beta H_0)/\text{Tr}(\exp(-\beta H_0))$ (i.e., the β-KMS state [33]) for large times t.

In an experiment, an external perturbation (e.g., an electromagnetic input) $b(t)$ is applied, changing the Hamiltonian H_0 to

$$H(t) = H_0 - b(t)B. \tag{5}$$

Here B could, for example, be the dipole moment operator, whereas the scalar function b could be a sine input, $b(t) = \sin(\omega t)$, or an appropriate pulse. Let us now expand the perturbed Karplus–Schwinger equation in powers of the perturbation $b(t)B$:

$$D(t) = D^{(0)}(t) + D^{(1)}(t) + D^{(2)}(t) + \cdots, \tag{6}$$

$$(\dot{D}^{(0)}(t) + \cdots) = \frac{1}{i\hbar}[H_0, (D^{(0)}(t) + \cdots)] - \Gamma\{(D^{(0)}(t) + \cdots) - D_\beta\}. \tag{7}$$

For a relatively small external perturbation b it is sufficient to consider the linear terms $D^{(0)}(t)$ and $D^{(1)}(t)$. Taking D_β as initial state, one arrives at

$$D^{(0)}(t) = D_\beta, \quad t > 0, \tag{8}$$

$$D^{(1)}(t) = \frac{1}{i\hbar}\int_0^\infty e^{-\Gamma\tau}e^{-i\tau H_0/\hbar}[-b(t)B, D_\beta]e^{+i\tau H_0/\hbar}\, d\tau. \tag{9}$$

If we take the output of our system to be the linear part $a^{(1)}(t)$ of the expectation value of some operator A

$$a^{(1)}(t) = \text{Tr}(D^{(1)}A), \tag{10}$$

we end up with a linearized input-output system: The input is given by $b(t)$ whereas the output can be brought into the form

$$a^{(1)}(t) = \int_0^\infty \Phi_{AB}(\tau)b(t-\tau)\, d\tau \tag{11}$$

with the integral kernel Φ_{AB} being

$$\Phi_{AB}(\tau) \overset{\text{def}}{=} \frac{i}{\hbar}\text{Tr}(D_\beta[e^{-i\tau H_0/\hbar}Ae^{+i\tau H_0/\hbar}, B])e^{-\Gamma\tau}. \tag{12}$$

The linearized input-output description (11) for a spectroscopic experiment is extremely simple and can easily be extended (by adding nonlinear terms, if the input b is taken to be large). Furthermore, it gives enough theoretical background for a

spectroscopist/engineer who sets up the actual experiment. Incidentally, the integral kernel Φ_{AB} can easily be determined experimentally as pulse-response to the input $b(\tau) \overset{\text{def}}{=} \delta(\tau)$. The spectrum (in the conventional sense) is the Fourier transform of Φ_{AB}.

Example

In a simple model of nuclear magnetic resonance the Hamiltonian of the unperturbed molecule is given by $H_0 = -\Omega \cdot S_z$, where $\Omega = g(1 - \sigma)B_0$, B_0 is the static magnetic field in z-direction, g the gyromagnetic constant of the respective nucleus, $\sigma \ll 1$ some screening factor, and S_z the spin operator in z-direction. The perturbation in x-direction is described by $V(t) = -b(t)S_x$, where $b(t)$ is some input function [e.g., proportional to a sine function or an appropriate pulse]. The response measured in the x- or y-direction is essentially the expectation value of S_x or S_y, respectively.

Now note the following important fact: The pulse response Φ_{AB} depends only on the thermal state D_β and *not* on a particular decomposition of D_β into pure states! Neither quantum jumps nor any other detailed dynamics on the pure-state level are necessary to describe a spectroscopic experiment in this statistical formalism. Conversely, determination of the spectrum (i.e., the Fourier transform of Φ_{AB}) does not tell us in which particular pure state (if any) the molecule under discussion actually is! Only information about the thermal density operator D_β can be extracted from the experimental results.

Though decompositions of the thermal density operator D_β (into pure states) do not play a role in this statistical formalism, one may *choose* some particular decomposition. One may, for example, consider the *spectral* decomposition of D_β into its eigenstates. The eigenstates of D_β coincide with the eigenstates Ψ_n of the unperturbed Hamiltonian H_0,

$$H_0\Psi_n = E_n\Psi_n, \quad \langle \Psi_n|\Psi_m \rangle = \delta_{nm}, \quad n, m = 1, 2, \cdots. \tag{13}$$

In order to get to Fermi's Golden Rule, one computes the average work $\bar{N}$ per second absorbed or emitted by the system (i.e., makes a power balance). To that end, the pulse-response Φ_{BB} is needed (input- and output operators B and A are identical). Expressing Φ_{BB} in the basis (13) leads to

$$\Phi_{BB}(\tau) = \frac{i}{\hbar}e^{-\Gamma t}\sum_n\sum_m p_n\{e^{i\omega_{nm}t} - e^{i\omega_{mn}t}\}|\langle \Psi_n|B\Psi_m\rangle|^2. \tag{14}$$

Here p_n are Boltzmann occupation numbers and $\omega_{mn} \overset{\text{def}}{=} (E_m - E_n)/\hbar$ are the frequencies for transitions between the eigenstates. At the present stage, these "occupied states" and "transitions" are *virtual* occupied states and *virtual* transitions, because in the original result (11) neither transitions nor any other dynamics of pure states played any role (see section 8 below).

The average power $\bar{N}$ exchanged between measuring device and molecule (depending on the frequency ω of the input and including a limit $\Gamma \to 0$) can then be expressed in the following way [103]:

$$\bar{N} = \sum_{n} \sum_{\substack{m \\ \omega_{mn} > 0}} p_n \frac{\pi}{2\hbar^2} |\langle \Psi_n | B \Psi_m \rangle|^2 \delta(\omega - \omega_{mn}) \hbar \omega_{mn}$$

$$- \sum_{n} \sum_{\substack{m \\ \omega_{nm} > 0}} p_n \frac{\pi}{2\hbar^2} |\langle \Psi_n | B \Psi_m \rangle|^2 \delta(\omega - \omega_{nm}) \hbar \omega_{nm} . \tag{15}$$

The first part of this formula refers to absorptions, the second to emissions. Interpreting eq. (15) again in the same "virtual" way as before, the obvious structure *Boltzmann factor × transition rate × energy* leads to transitions rates

$$W(n \to m) = \frac{\pi}{2\hbar^2} |\langle \Psi_n | B \Psi_m \rangle|^2 \delta(\omega - |\omega_{nm}|) , \tag{16}$$

which is Fermi's Golden Rule [53].

It might well be that a detailed investigation of individual quantum processes shows that this sort of setting is not only virtual but also "true" (cf. section 8). If some initial state decays into a continuum of states [27,61], for example, decay probabilities can be rigorously derived. In the general situation considered here, Fermi's Golden Rule is one of many possible *interpretations* of the input-output result (11) in individual *diction*. In eq. (11) neither transitions nor transition probabilities play a role. Using a different decomposition of the thermal density operator (i.e., not the spectral one) will lead to a completely different picture on the pure state level.

Hence Fermi's Golden Rule gives conditional probabilities in the following sense: *Under the condition* that one interprets spectroscopy by jumps between eigenstates of the unperturbed Hamiltonian H_0, the transition probabilities are given by eq. (16). In particular, initial and final states of a quantum jump are always (stationary) eigenstates of the unperturbed Hamiltonian H_0.

Summarizing: Spectroscopy of ensembles of molecules can only give information about the thermal non-pure state D_β and *not* about the decomposition of D_β into pure states. Therefore one has a certain freedom in decomposing the thermal non-pure state into pure states. One could, for example, decompose the thermal state of a molecule into (non-stationary) pure states in such a way that the nuclei are localized as much as possible. Though this proposal is not worked out here, it gives some feeling for the approach of the present paper: Starting from the statistical version of quantum mechanics (in terms of density operators), it is tried to get to a best estimate of pure state behaviour (here pure states are not necessarily thought to be eigenstates of the molecular Hamiltonian). This estimate of pure state behaviour can then be taken as starting point to discuss spectroscopy of single molecules. In single-molecule spectroscopy more information than just eigenvalues and transition probabilities can be obtained.

4. Spectroscopy of single molecules

Looking at the status of experimental techniques without prejudice, one can only be amazed at the fantastic achievements reached there. It is almost a miracle that experiments with single (or few) photons [20,21,66] and single (or few) molecules or ions [24,86,116,137] can actually be done.

The theoretical interpretation of these experiments is on an extremely sophisticated level. It is surprising that often single-atom experiments can be interpreted by the traditional quantum-mechanical formalism (including the projection postulate) [39] or even by completely classical explanation schemes [113,152].

The present paper is an attempt to understand why these explanations work so surprisingly well. To this end, let us try to use the (linear) response theory of section 3 for single-molecule spectroscopy. Then an important point cannot be accepted any more: In eq. (10) it was implicitly claimed that the output observable A can be measured *without disturbing the state of the system itself*. This would certainly be nonsense if the actual state were unstable, but could be accepted if the pure state in question (or an ensemble of pure states) were stable under a small external perturbation. In the statistical approach (where the expectation value of the thermal non-pure state D_β is concerned), one can be quite confident that stability is no problem. For single-molecule spectroscopy (described in terms of pure states) the situation is very different: arbitrarily chosen pure states are changed during a "measurement" and hence it is important to have stable states; or stable ensembles of pure states.

Even with stable states or stable ensembles of states one must be prepared to get a stochastic behaviour (see section 8): To get an impression, the very nice and concise paper by W.P. Ambrose and W.E. Moerner [18] (cf. [43,62,63,81–84, 88,97,98,141,142]) is recommended. Ambrose and Moerner investigate pentacene substitutional impurities in a *p*-terphenyl crystal. Depending on the particular orientation of the pentacene impurity, fluorescence excitation spectroscopy gives rise to varying peaks in the spectrum. The homogeneous line width of individual pentacene defects is about 7.5 MHz, whereas the inhomogeneous line width is about 2–42 GHz. For *single-molecule spectra*, the laser used may be tuned far into the wings of the inhomogeneous line, where the number of defects per homogeneous width is less than one, that is, where non-overlapping individual pentacene defects may be found (if the overall concentration of pentacene defects is low enough, approximately 6.6×10^{-8} mol mol^{-1}). For individual "defects of class II", the position of the line differs from scan to scan, changing some few hundreds megahertz. This "spectrally migrating, stochastic" behaviour of class II can be explained the following *classical* way: A single pentacene molecule in the *p*-terphenyl matrix will be influenced by the surrounding matrix molecules. Hence depending on this particular influence (e.g., the particular occupied eigenstates of the neighbouring molecules) the level splitting of the pentacene molecule will change

and lead to different spectroscopic lines. The pentacene molecule is a kind of probe testing different environments in the solid crystal.

This is a very useful interpretation, since it works almost perfectly well [18,152], even in more complicated cases [151]. It is called *classical,* because the influence of surrounding molecules onto the single pentacene defect is taken into account only through changes in some parameters of the pentacene molecule, e.g., changes in the level splitting of a certain spectroscopic transition of pentacene. Only the pentacene defect itself is treated quantum-mechanically. In a full quantum-mechanical description of the joint system {pentacene molecule & environment of *p*-terphenyl molecules} things change dramatically, because the states of this joint system are not necessarily product states. The composition rule for joining pentacene and *p*-terphenyl molecules is then quantum-mechanical and not classical as before. In such a description, the thermal non-pure state D_β would refer to the mentioned joint system and not to the pentacene molecule alone. One could then, of course, try again to start with a response theory. The problem with such a quantum-mechanical explanation using response theory is that stochastic behaviour cannot easily be incorporated [136]. This stochastic behaviour (in the experiment of Ambrose and Moerner) is a consequence of the consideration of single molecules and "averaged out" for an ensemble of molecules. Anyway: Spectroscopy of single molecules (coupled to some environment such as a matrix of neighbouring molecules and/or coupled to the radiation field) gives more information than just (differences of) eigenvalues and transition probabilities.

Quite generally, the dynamics on the level of density operators is regular, whereas the dynamics on the pure state level can be stochastic and nonlinear (see section 8) [13,14,57–59,100–102]. Averaging over a particular stochastic dynamics on the pure state level gives back the regular density operator dynamics [136]. Hence statistical quantum mechanics (in the sense of density operators) can give a picture which is very different from individual-statistical quantum mechanics (using pure states). Only the latter individual formalism (see section 5) says something about the behaviour of individual single quantum systems. Single-molecule spectroscopy, in particular, cannot be discussed in the usual quantum formalism (in terms of density operators).

Here "single-molecule spectroscopy" is always meant in the sense *spectroscopy of the quantum joint system {single molecule & environment}.* The environment could, for example, consist of the radiation field or the matrix in which the single molecule is embedded (or both). The question *"What is the influence of the molecular environment?"* [8–12,55,56,95,109,119,120,129,130,139,140,143–149] will always be important background for the discussions in this paper, even when it is not explicitly mentioned. Hence all the questions posed below refer to "isolated" single molecules as well as to the joint system {molecule & environment}, even when they are only formulated for "isolated" single molecules. A proper discussion of the *influence of the molecular environment* is difficult and not intended here. A keyword would be: dressing procedures [22].

Starting from an entirely quantum-mechanical situation, it would be interesting to know how classical structures arise and why classical viewpoints are so successful even in spectroscopy of small single molecules. The result of this paper will be that the *requirement of stability (of decompositions into pure states) gives rise to classical structures*. In this and the following sections this point of view will be developed in a leisurely way.

The following question serves as a starting point: "What happens to a molecule during spectroscopic measurement and which role is played by the eigenstates of the molecular Hamiltonian?" There are essentially two differing points of view postulating what happens to a molecule during measurement:

- Starting from an arbitrary initial state, the molecule is transformed into an eigenstate of the unperturbed molecular Hamiltonian H_0. Transitions between these eigenstates occur with transition rates given by Fermi's Golden Rule (16). Here this will be called the *Bohr–Einstein point of view*.

- Starting from an arbitrary initial state, the molecule is transformed into an "eigenstate" of the coupling operator (which was called B in section 3). Here this is called *von Neumann's point of view*. The term "eigenstate" (of the coupling operator) has been put into marks, since the spectrum of the coupling operator is usually continuous and not discrete.

Von Neumann's point of view is usually taken when the quantum measurement process is discussed in detail, replacing quantum jumps by a quantum diffusion of pure states [38,59,60,100,101,150]. For a two-level molecule such a quantum diffusion can be visualized on the surface of the sphere in three-dimensional space (see fig. 6): If the Hamiltonian of the two-level system is, for example, proportional to σ_1, and the dipole moment operator given by $B := \sigma_3$, an initial (pure) state "walks" to the poles of the sphere which correspond to eigenstates of σ_3. Von Neumann's point of view is quite plausible, since the "only" influence from the experimenter comes in via the coupling operator B (at least in the linear response scheme).

The Bohr–Einstein point of view, on the other hand, is usually taken in spectroscopy. Fortunately, it is surprisingly simple and leads quickly to interesting results.

The two points of view cannot easily be reconciled. With respect to the Bohr–Einstein point of view it is the molecular energy which is "measured"; with respect to von Neumann's point of view it is the dipole moment which is "measured". It is therefore legitimate to ask *what happens to a molecule during spectroscopic measurement?* As shown in section 3, one cannot answer this question experimentally by usual spectroscopic methods (applied to many molecules): Only the spectrum itself (i.e., transition frequencies and transition probabilities) can be determined, but not the actual states of the investigated molecules.

Let us therefore postpone this problem to section 8 and ask the question "in which pure state is a molecule?" in a slightly different context, replacing for the

moment the molecule by one litre of water [4] (which surely could be investigated by spectroscopic means). The non-pure thermal state [5] for this litre of water will again be called D_β and one might well expect, that the linear response theory of section 3 works. The question now is: "In what pure state is this litre of water *really?*" As far as these questions are concerned, there is no principal difference between a single molecule and a single litre of water. The main reason for taking such a "strange" example is just to make clear that we deal with *one single* system (being in a pure state) and not with an ensemble in the sense of Gibbs (in particular, one should not think of the water as an ensemble of water molecules; the water molecules interact strongly! Also the pure state in question refers to the litre of water as a whole). Hence here the raison d'être for the non-pure thermal state D_β is our limited knowledge about the (unstable, quickly changing) pure state of the water system. Hence we actually deal with a kind of ensemble in time (since the pure state changes).

Now again: What is the pure state of a litre of water? The answer comes from an appropriate decomposition of the thermal state with density operator D_β into pure states,

$$\mathrm{Tr}(TD_\beta) = \int_{\text{all pure states }\phi} \phi(T)\mu(d\phi) . \tag{17}$$

Here T is an arbitrary observable of the litre of water and $\phi(T)$ is the expectation value of T with respect to the pure state ϕ. Every pure state of the system can be represented by some state vector Ψ_ϕ (where the phase is only fixed up to some complex number of modulus 1) by

$$\phi(T) = \langle \Psi_\phi | T\Psi_\phi \rangle , \tag{18}$$

and vice versa [6]. The probability to find a pure state in some set of S of pure states is given by $\mu(S)$ (hence μ, in mathematical terms, is a probability measure). Equation (17) corresponds precisely to the decomposition in eq. (3). There the measure is given by $f(\vartheta, \phi) \sin \vartheta \, d\vartheta \, d\phi / 4\pi$ and the probability to find the pure state in the set S of pure states (S is some part of the surface of the sphere) is given by

$$\int_S f(\vartheta, \phi) \frac{\sin \vartheta \, d\vartheta \, d\phi}{4\pi} . \tag{19}$$

The more "complicated" way of formulating eq. (17) is only due to the fact that here one has no simple parametrization of the pure states (as by spherical coordinates).

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[4] For this example, the Hamiltonian and the respective thermal state D_β refer to all molecules in the litre of water and their interactions. The translational energy of the centre of mass has been separated.

[5] The set of all (not necessarily pure) states and the set of density operators are in 1-1 correspondence.

[6] This is true if an irreducible representation of the observables is chosen, which is the usual situation.

The important point is: As illustrated in section 2, the decomposition (17) is not unique. Let us, for example, choose the spectral decomposition of D_β into (stationary) eigenstates (see eq. (13)),

$$\text{Tr}(TD_\beta) = \sum_n p_n \langle \Psi_n | T\Psi_n \rangle . \tag{20}$$

If this decomposition is only used as a mathematical tool to investigate the density operator, e.g., compute transition probabilities, one does not have any conceptual problems at all. But *if it is taken as physically relevant*, i.e., if the litre of water is thought to actually be in one of the eigenstates Ψ_n with probability p_n, it *would mean that one litre of water is always in a stationary state*. Physical intuition tells us that this is absurd: "Water molecules move and hence a litre of water is never in a stationary state."

The concept of "moving water molecules" is, of course, a classical one! Hence the whole argument is slightly inconsistent, since we start with a quantum description and would like to derive (approximate) classical behaviour. Hence here the final desired result is already used in a heuristic way.

Let us now leave the far-fetched example of water and turn back to molecules. Again there is no a priori reason to expect a single molecule (the translational energy being separated) to be in eigenstates of the underlying molecular Hamiltonian. Also a spectroscopic measurement does not necessarily lead to eigenstates of the Hamiltonian (see the discussion above on the Bohr–Einstein vs. the von Neumann point of view).

Usually, eigenstates of some Hamiltonian are rather unstable under external perturbations [17] and therefore replaced by coherent states [93] or "localized eigenstates" as in a Born–Oppenheimer description. These descriptions are more *stable* under small external perturbations. To give an example: When the surface of a solid is observed with a raster tunnel microscope (which is an observation instrument but also an external perturbation), one does not expect to see molecular eigenstates, but wave packets. Here we try to obtain a more general understanding of stability of pure states, which also gives an alternative approach to decoherence, coherent states and the Born–Oppenheimer scheme. At the present stage, the particular sort of the external perturbation (electromagnetic or gravitation field, collisions with neighbor molecules, etc.) is not taken into account.

Illustrating this facts from different points of view one can show at the same time the *ingenuity of the Born–Oppenheimer idea of a nuclear structure*: Consider a molecule with internal Hamiltonian H_0 (the kinetic energy of the center of mass being subtracted). Let, furthermore, I denote the unitary operator which implements space inversion

$$I\Psi(q_1, \cdots, q_L; Q_1, Q_2, \cdots, Q_M) \stackrel{\text{def}}{=} \Psi(-q_1, \cdots, -q_L; -Q_1, -Q_2, \cdots, -Q_M) .$$
$$\tag{21}$$

Here the q's are electronic coordinates and the Q's are nuclear coordinates. If the Hamiltonian H_0 does not contain the weak neutral current terms [107,108], it is invariant under space-inversion, i.e.,

$$IH_0I^{-1} = H_0 . \tag{22}$$

Then the eigenstates Ψ_n of H_0 (see eq. (13)) can be chosen to be symmetry-adapted,

$$I\Psi_n = \pm\Psi_n , \quad n = 1, 2, 3, \cdots , \tag{23}$$

and therefore will always fulfill

$$\langle \Psi_n | Q_j \Psi_n \rangle = \langle I\Psi_n | Q_j I\Psi_n \rangle = \langle \Psi_n | I^{-1} Q_j I \Psi_n \rangle = \langle \Psi_n | - Q_j \Psi_n \rangle = 0 ,$$

$$j = 1, 2, \cdots, M . \tag{24}$$

This is quite strange, since then

- a nuclear molecular frame does not exist,

- different isomeric molecular forms do not arise,

- and a sequence of monomers in a macromolecule does not make sense,

since nuclear frame, isomerism and sequential structure in a macromolecule need (at least approximately) localized nuclei, which is incompatible with the result of eq. (24).

Why should the Born–Oppenheimer idea of a nuclear structure be used? Heuristically, care is taken to choose stable states instead of (symmetry-adapted) eigenstates. To this end, one takes "eigenstates" within all the particular minima of a given Born–Oppenheimer potential, called "localized eigenstates" above. These "localized eigenstates" are stationary only in an approximate way [7], but can nevertheless be more stable under small external perturbations than the strictly stationary eigenstates (23) of the molecular Hamiltonian in question. It is, of course, not an easy task to substantiate this heuristic point of view mathematically. The present paper is an attempt to develop a formalism of quantum mechanics which should eventually lead to a rigorous mathematical proof (and also to "corrections" of the usual BO-picture).

What is the interesting point with the Born–Oppenheimer idea of a nuclear structure? If it is seen as an *approximation*, one might try to improve it, finally ending up with the exact eigenstates of the Hamiltonian H_0, which would distroy the whole BO-approach. Hence it is important to see the BO-approach as being qualitatively different from quantum mechanics. One should *not* try to improve BO-results ad

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[7] "Stationary" refers to the dynamics implemented by the Hamiltonian H_0 of the molecule itself, in contrast to "stability under external perturbations". An ammonia molecule in a "handed" state, for example, is not stationary at all due to the high tunneling frequency.

infinitum. Though this would give better results for the eigen*values* and transition probabilities (and in many cases better agreement with experimental spectra), one would end up with the physically questionable (strictly stationary but unstable) eigenstates of H_0. In other words: the interesting aspect of the Born–Oppenheimer approximation is that the approximation is in a way better than the exact result. In the present paper we try to understand stability requirements and lay the foundation for finding a "best possible BO-approximation". In particular, a strict distinction will be made between eigen*values* and eigen*states*: Eigenvalues are quite stable under perturbations [72], whereas eigenstates are (often, but not always!) unstable. But note that it could well be that the formalism proposed here leads to approximate eigenstates in certain "quantum" cases. It should *not* be understood as a propaganda against using eigenstates in *any* situation. Ammonia-type molecules serve as the phenomenological background of this investigation: Ammonia behaves, in a way, much more quantum-mechanically than chiral molecules. The important point will be to understand this and similar "phase transitions".

Summarizing: The choice of a decomposition of the thermal non-pure state D_β should be done in such a way that the resulting ensemble of pure states is stable under small external perturbations. Surely, not all the mathematically possible external perturbations are physically relevant. Nevertheless, at the present stage, no particular class of "physically relevant external perturbations" will be fixed. It will be made plausible in section 5 that the requirement of stability leads to a *unique* decomposition of thermal non-pure states into pure ones. This result might change if the class of external perturbations is very much restricted.

An ensemble of pure states is thought to describe the statistics of (many distinguished) single molecules, all in pure states, and all accessible to individual spectroscopic investigation. Coupling an external perturbation to these molecules (modelled, e.g., by white noise), one will get a stochastic dynamics on the level of pure states (see section 8).

- In case the original distribution of pure states was stable, it will not change much under this external influence.

- In case the original distribution of pure states was unstable, it will approach a stable distribution after some transient time.

Here "distribution of pure states" is meant in the sense of fig. 3, described by some probability density $f = f(\vartheta, \phi)$ (for the special case of 2×2-matrices, and similarly otherwise).

Note that the notion "ensemble" (of pure states) is not an ensemble in the sense of Gibbs. It may also describe a (not necessarily large) number of (distinguished) individual similar systems in given pure states, i.e., I allow myself to be rather unprecise about these more "philosophical" points [8].

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[8] In mathematical terms, an ensemble is a probability measure on the space of pure states.

We deal now with two different sorts of statistics:

- Statistics of pure states for quantum theory in individual setting. This statistics is described by a probability distribution on the set of pure states (see fig. 3).

- Statistics in terms of *one* non-pure state for quantum theory in statistical setting. This is the usual formalism of quantum mechanics.

Every probability distribution on the set of pure states gives rise to some non-pure state (density operator) via eq. (17), but the converse is not true, since a non-pure state (density operator) cannot be uniquely decomposed into pure states (see section 2).

5. An individual setting of quantum mechanics

Let us go through the same line of arguments again, using yet another example, namely a magnet built up from a big (but finite) number of quantum spins. For a given inverse temperature β there exists precisely one thermal non-pure state (i.e., β-KMS state) with density operator

$$D_{\beta,0} = \frac{e^{-\beta H_0}}{\mathrm{Tr}(e^{-\beta H_0})} . \tag{25}$$

Here H_0 is the Hamiltonian of this magnet (in zero external field). Most "hard facts" like the heat capacity, for example, are already encoded in these density operators $D_{\beta,0}$, $\beta > 0$, and do not depend on the particular decomposition of the density operator into pure states. Different decompositions of a given density operator $D_{\beta,0}$ into pure states can give rise to completely different theories [23,80]. One may, for example, decompose it into symmetry-adapted eigenstates of the Hamiltonian H_0. These symmetry-adapted eigenstates have zero specific magnetization. Therefore in such a theory permanent magnetism (in zero external magnetic field) would not occur. On the other hand, we could try to decompose the density operator $D_{\beta,0}$ into pure states in such a way that the expectation value m of the specific magnetization operator $\hat{m}$ is not exactly zero, but distributed around two values $\pm m_\beta$, and therefore leading to nonzero specific magnetization (for $\beta > \beta_{\mathrm{crit.}}$, i.e., for a temperature below the Curie point).

Remark
The zero-field situation considered here is, of course, entirely artificial. A small change of the magnetic field B can change the thermal state dramatically. Here it is tried to understand this instability and give sense already to the zero-field situation, e.g., compute the permanent magnetization in the zero-field situation and not for small external magnetic field B. For single molecules discussed in section 9, the situation is similar. An isolated molecule is an artificial object, with strange proper-

ties as in eq. (24). In the situation of single molecules, it is not so clear what sort of external perturbations (corresponding to the magnetic field B) should be considered.

The m-distributions of two different decompositions of $D_{\beta,0}$ into pure states are sketched in fig. 4. In one case, m is distributed around $m = 0$, whereas in the other m is distributed around two different values $\pm m_\beta$. Both decompositions are compatible with one and the same density operator $D_{\beta,0}$ (compare fig. 3). Hence the density operator of a thermal state does not necessarily tell us something about the individual behaviour of a magnet built up from a finite number N of spins. The philosophy behind this line of arguments is the following: The single individual magnet is actually in a pure state. This pure state is usually not known and hence one has to consider statistics of pure states. The problem is to find the correct statistics of pure states compatible with the thermal density operator $D_{\beta,0}$ (i.e., it is necessary to find a stable decomposition of $D_{\beta,0}$ into pure states; compare the discussion of two different sorts of statistics at the end of section 4). If this stable distribution has several "peaks" (as the two peaks in the right part of fig. 4), magnetization is an approximate classical observable (with values $\pm m_\beta$). The sharper the peaks, the more classical the situation becomes.

Let us, for a moment, turn back to the decomposition of $D_{\beta,0}$ into symmetry-adapted eigenstates. Then one might argue with good reasons, that this *decomposition* into symmetry-adapted eigenstates is unstable under small external perturbations:

- Introducing, for example, a small external magnetic field B into the Hamiltonian H_0 will change the situation completely. The respective density operator $D_{\beta,B}$ will have a nonzero expectation value of the magnetization operator (even for small B, if the temperature is below the Curie temperature) and it will therefore not be possible to decompose it into pure states with magnetization zero.

- Consider a Monte Carlo simulation of a magnet [26,131]. There the Hamiltonian dynamics is replaced by some "artificial" Glauber-type dynamics, which does not leave the set of symmetry-adapted eigenstates invariant: Any
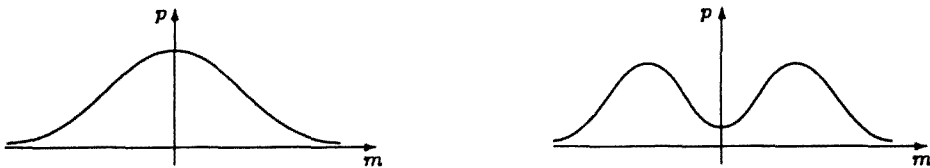

Fig. 4. Different distributions p of the specific magnetization referring to different decompositions of the same density operator (25) into pure states. This figure refers to some fixed inverse temperature $\beta > \beta_{crit}$ and some fixed number N of spins. The figure is qualitative and not based on a calculation.

symmetry-adapted eigenstate is transformed into a non-stationary state already under the first step of the Glauber dynamics.

Therefore we meet again a situation where it does not make sense to restrict oneself to eigenstates. This is not to mean that eigenstates should never be used!

Consequently, *different decompositions of a non-pure state are not at all physically equivalent*. Some of them are stable ($\equiv$robust) and some are unstable (under external perturbations) and the task is to find out the robust ones. In the example of the magnet, it is rather simple to find appropriate external perturbations (namely a small external field, perhaps varying stochastically in space and time). In the example of a molecule, the situation is much more involved. It might indeed be necessary to investigate the influence of the (quantum) electromagnetic field, i.e., to investigate the joint system {molecule & radiation field}. For such cases one would like to have an appropriate decomposition at hand which guarantees robustness of the respective decomposition into pure states even if it is not clear what the specific external perturbations are.

Let us think of statistical mechanics and illustrate the situation by means of the famous gedankenexperiment of Borel [31,p. 98]. There the influence of a Sirian beetle (8.3×10^{16} m away) on a gas at normal conditions in a cube of 10 cm length is estimated. The beetle's walk of just 1 cm changes the (classical-mechanical) computation such that the position of an individual particle is changed by approx. 10 cm after 10^{-6} seconds. The individual (classical-mechanical) pure states are very unstable. That is the reason for choosing a *stable ensemble* of (unstable) individual states, namely the Gibbs ensemble, characterized by the maximal-entropy principle of Jaynes.

With Jaynes' principle of maximal entropy [70] in mind, it is clear what has to be done to get robust decompositions of thermal non-pure states. One simply chooses the decomposition having maximal entropy with respect to equipartition of pure states (i.e., with respect to the unique ensemble of pure states invariant under all potential symmetries of the system in question; hence "equipartition" is *not* equipartition of eigenstates, but equipartition of *all possible* pure states!). Therefore, to apply Jaynes' principal of maximal entropy, one needs two ingredients,

- an equipartition of pure states [9],

- and an entropy for a given (arbitrary) distribution of pure states with respect to equipartition.

For simplicity, let us consider a two-level system. The *pure-state space* of the two-level system can be represented as the surface S_2 of a sphere in three-dimensional real space (see Appendix 1 and fig. 3). The potential symmetries (corre-

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[9] For infinite-dimensional Hilbert spaces, an equipartition measure on the space of pure states does not exist. This problem is not discussed here.

sponding to the unitaries and antiunitaries acting on the 2-dimensional Hilbert space) are represented as rotations and reflections in 3-space. The unique invariant measure μ_{eqp} (equipartition of pure states) on S_2 is then given in spherical coordinates by $\mu_{\mathrm{eqp}} = \sin\vartheta \, d\vartheta \, d\phi/4\pi$. The entropy $S(\mu)$ of a given ensemble

$$\mu = f(\vartheta, \phi) \frac{\sin\vartheta \, d\vartheta \, d\phi}{4\pi} , \tag{26}$$

on the other hand, is defined by

$$S(\mu) = S(\mu|\mu_{\mathrm{eqp}}) = -\int_{S_2} f(\vartheta, \phi) \, \ln[f(\vartheta, \phi)] \frac{\sin\vartheta \, d\vartheta \, d\phi}{4\pi} , \tag{27}$$

i.e., as its relative entropy with respect to the equipartition μ_{eqp}. These definitions of equipartition and entropy can be generalized to arbitrary $d \times d$-matrices. The equipartition measure, in particular, is the canonical measure on the d-dimensional complex projective plane [73,94]. Here for most considerations the 2×2-matrices will be used to simplify understanding.

The maximum-entropy principle can then be formulated as follows: *Assume that a given quantum system is in a pure state but that this pure state is unknown. Assume furthermore that the* only *knowledge about the system is some non-pure state with density operator D. Then the probability of finding the pure state in some subset of all pure states is described by the ensemble of pure states having maximum entropy with respect to equipartition.* The ensemble with maximum entropy is chosen among all the ensembles of pure states yielding the given density operator D (via mixing in the sense of eqs. (3), (17)).

Remarks

- If an ensemble of pure states if of the form $(f(\vartheta, \phi) \sin\vartheta \, d\vartheta \, d\phi/4\pi)$, i.e., of the form *function f on the space of pure states × equipartition measure*, it is called *absolutely continuous with respect to equipartition measure* in mathematical terminology. The definition in eq. (27) holds only for such absolutely continuous ensembles, whereas for all other ensembles the entropy is minus infinity ($-\infty$) [45,46]. A decomposition of a density operator into its eigenstates, in particular, has entropy $-\infty$, and not maximal entropy.

- Let us look at fig. 4. A decomposition of the thermal state (25) into eigenstates leads to a distribution similar to the left part of the figure (sharply peaked at $m = 0$). A decomposition of the thermal state (25) according to the maximum-entropy principle, on the other hand, has a tendency to lead to the distribution in the right part of the figure (because the maximum-entropy condition tends to distribute the expectation values of m the best possible way among all potential values $m \in [-1, +1]$, and not to concentrate it on one particular value as, e.g., $m = 0$). A mathematical argument will be given below.

- To apply Jaynes' principle of maximum entropy, "every" available information has to be included. Since one knows, for example, the precise Hamiltonian for the joint system {molecule & radiation field}, one should discuss this joint system to understand spectroscopic phenomena. Such an investigation can, of course, lead to the result that the radiation field does not play any role for *certain* spectroscopic phenomena. For a detailed investigation of spectroscopic phenomena in every respect, the consideration of the quantum radiation field is necessary (think of the spontaneous decay of excited states).

- Pure states do *not* necessarily make sense for arbitrary systems (and in such a case it is not advisable to decompose thermal states into pure states). If a system is strongly entangled with its environment (i.e., Einstein–Podolsky–Rosen-correlated with its environment), then it does not make any sense to view it as being in a pure state. In this case either the environment has to be included into the description (e.g., by passing from the isolated molecule to the joint system {molecule & radiation field}, as before) or one must find a suitable dressing transformation [22]. A dressing transformation changes the splitting within a joint system in such a way that the EPR-correlations (almost) disappear. A dressed molecule, for example, can then be treated as being in a pure state.

- A "mixed" state can have different meanings [17,48]: It can either be a shorthand description of an ensemble of pure states, or arise as restriction of a pure state (e.g., of the joint system {molecule & radiation field}) to a smaller part (e.g., the molecule). In the latter case, it does not necessarily make sense to decompose the "mixed" state into pure states (or only after an appropriate dressing transformation). Here the term "mixed" state is always replaced by *non-pure* state.

- It is important not to confuse different concepts of entropy. The von-Neumann entropy $\mathrm{Tr}(D \ln D)$ of a density operator D [87,138], for example, is not identical with the entropy of its decomposition into pure states as defined in eq. (27). Further entropies are used below. In the present paper, the relations between these entropies will not be discussed.

- Maximal entropy ensembles can be shown to be of the form

$$\frac{\exp\{-\beta\phi(\tilde{H})\}\ \mu_{\mathrm{eqp}}}{\int_{\text{all pure states }\phi}\exp\{-\beta\phi(\tilde{H})\}\ \mu_{\mathrm{eqp}}(d\phi)}\ , \tag{28}$$

where $\tilde{H}$ is some linear selfadjoint operator, usually not coinciding with the original Hamiltonian H_0 used to construct the thermal non-pure state as in eqs. (2), (25). The measure μ_{eqp} is the equipartition ensemble of pure states.

- The formalism here is based on Kolmogorov axiomatic probability theory and it is not clear at all if "nature", when behaving "randomly", should behave

according to these axioms [71]. The notion of probability is particularly delicate in quantum mechanics.

Let us try to reformulate what we have done till now: Instead of decomposing a thermal density operator into eigenstates, a maximal entropy decomposition into non-stationary states was used. This maximal entropy decomposition may give rise to an approximate classical structure, as suggested in the right part of fig. 4: Most of the pure states in the chosen ensemble have approximate expectation values $\pm m_\beta$ of the specific magnetization operator $\hat{m}$. Nevertheless one has still pure states in the maximum-entropy ensemble with expectation value *zero* of $\hat{m}$. The superposition principle is still fully valid, i.e., arbitrary superpositions of given states are still legitimate states of the system in question (a magnet in our example). Hence it is also legitimate to superpose some pure state (with state vector Ψ) and its space-inversed form ($I\Psi$, similar as in eq. (21)), to end up with a state having *zero* expectation value of $\hat{m}$. Such states still arise in the ensemble chosen (because the respective density p is nonzero at $m = 0$). But states with expectation value $m = 0$ only arise with low probability. Therefore such states are unstable under external perturbations and decay preferably into states having expectation value $\pm m_\beta$. Hence in the present formalism dynamical aspects come in and there is no one-to-one correspondence any more between classical observables and superselection rules as in algebraic quantum mechanics [33,34,99,117] (because strict classical observables and superselection rule do not exist in the formalism advocated in the present paper).

In this paper, maximum-entropy decompositions of some given thermal non-pure state (for a given number N of spins, e.g., for 1 spin [121,122], or some given number of modes of the radiation field coupled to some molecule) will not be computed in an explicit way.

Another important new aspect is brought into discussion and should be emphasized: What happens when the number of degrees of freedom increases [15,16]? Interestingly enough, the solution to this question offers the possibility to discuss "how fast" classical observables arise with an *increasing but finite* number of degrees of freedom (and not in time).

Let us try to illustrate this point for a magnet consisting of N quantum spins. Let $D_{\beta,N}$ be the density operator (for zero external field) and consider its maximum-entropy decomposition $\mu_{\max} = f_{\beta,N}(\phi)\mu_{\mathrm{eqp}}^N(d\phi)$, where $\mu_{\mathrm{eqp}}^N(d\phi)$ is the equipartition measure on the space of pure states [10] and where $f_{\beta,N}$ is the probability-density function on the pure-state space [ϕ stands for an arbitrary pure state, which may be implemented by some state *vector* ψ_ϕ, if this is helpful: $\phi(\cdot) = \langle \psi_\phi | \cdot \psi_\phi \rangle$]. Consider now the probability $P_{\beta,N}[m_1, m_2]$ to find the expectation value $\phi(\hat{m}_N)$ of the mean-magnetization operator $\hat{m}_N$ in the interval $[m_1, m_2]$ (all being written in one dimension, for simplicity) with respect to the ensemble $f_{\beta,N}(\phi)\mu_{\mathrm{eqp}}^N(d\phi)$ of pure

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[10] The equipartition measure is $\sin\vartheta \, d\vartheta \, d\varphi$ in case of a two-level system. For $m \times m$-matrices, a more general expression can be given by means of generalized spherical coordinates.

states. This probability $P_{\beta,N}[m_1, m_2]$, for varying intervals $[m_1, m_2]$, is all we need. The connection between this probability measure P and the probability densities p (or more precisely $p_{\beta,N}$) sketched in fig. 4 is (by definition) given as

$$P_{\beta,N}[m_1, m_2] = \int_{m_1}^{m_2} p_{\beta,N}(m) \, dm \, . \tag{29}$$

Roughly spoken, an *approximate classical observable* gets "more and more classical" if the probability $P_{\beta,N}$ or the respective probability density $p_{\beta,N}$ gets more and more concentrated on certain values for the magnetization, say $+m_\beta$ and $-m_\beta$, *with increasing N* (see section 6). If neither $+m_\beta$ nor $-m_\beta$ is in the interval $[m_1, m_2]$, then the respective probability $P_{\beta,N}[m_1, m_2]$ dies out. Usually (i.e., if $\beta \neq \beta_{crit.}$) this takes place exponentially (see section 6),

$$P_{\beta,N}[m_1, m_2] \sim \exp\left\{ -N \inf_{m \in [m_1, m_2]} (s_{mean}(m)) \right\} \, . \tag{30}$$

In this formula, $s_{mean} = s_{mean,\beta}$ is a (positive) entropy (taking as its minimum the value zero, see fig. 5) in the sense of the large-deviation formalism [45,46,76] ("large" deviations means that these deviations "die out" with increasing particle number N, whereas normal thermal fluctuations are proportional to $\sqrt{N}$.). It has the form of a double-minimum potential (see fig. 5) and describes the successive concentration of the (expectation vales of the) magnetization operator to the specific values $+m_\beta$ and $-m_\beta$ with increasing number of spins considered (the entropy function takes its minimum zero at $+m_\beta$ and $-m_\beta$). Other expectation values of the magnetization operator are still possible, but die out with increasing N. In other words: *this entropy function s tells us "how quickly" classical observables arise with increasing number of spins.*

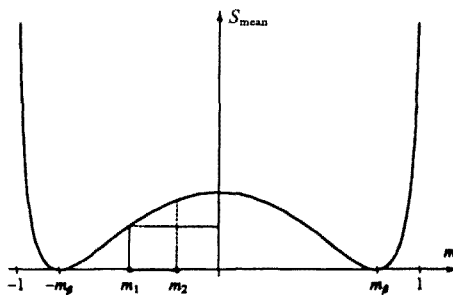As mentioned earlier, the superposition principle still holds universally for

Fig. 5. An entropy function s_{mean} in the sense of fluctuation (large-deviation) theory, describing how fast the mean magnetization of a spin system gets classical with an increasing number of spins. The figure is based on an approximate calculation in section 6 for the Curie–Weiss model. The temperature is fixed and has been taken here as one third of the critical (Curie) temperature. Above the Curie temperature the respective entropy s_{mean} would only have one minimum, namely at $m = 0$.

finitely many degrees of freedom N (see remarks in the second paragraph of this section). But *after the limit* $N \rightarrow \infty$, only pure states having expectation values $\pm m_\beta$ "survive", and all others "die out" according to eq. (30). Pure states having specific mean magnetization zero, $m = 0$, do not exist any more. In particular, superpositions of a pure state Ψ and its space-inversed form ($I\Psi$, similar to that in eq. (21)) are "forbidden" after the limit $N \rightarrow \infty$ and the mean magnetization $\hat{m}$ becomes a *strict* classical observable, now equivalent to a superselection rule.

Remarks

- Classical observables are not defined here in a formal way, since formalization at too early a stage is not helpful for a new approach to quantum theory. The essential point with a strict classical observable C (such as the magnetization $\hat{m}$ in the limit $N \rightarrow \infty$) is that superpositions of its eigenstates cannot be superposed any more. In the present paper's formalism, such superpositions do still exist for finite N, but with low probability (with respect to the maximum-entropy ensemble of a thermal state). It is not a priori clear, that low probability with respect to a maximum-entropy ensemble is equivalent to quick decay in time (but see the discussion in section 7).

- One should clearly distinguish between all the different entropies used in this paper: The von Neumann entropy of a density operator; the entropy of an ensemble of pure states with respect to equipartition; and the entropy s_{mean} describing how fast a classical observable arises with increasing number N of degrees of freedom.

- According to mathematical convention [45,46], the entropy s_{mean} has been chosen as a positive function.

- Equation (30) refers to the distribution of the *expectation values* $\phi(\hat{m}_N)$ in the ensembles $f_{\beta,N}(\phi)\bar{\mu}_N(d\phi)$. This restriction to *expectation values* is unnecessary and only chosen here for simplicity. A more general discussion would, for example, include distributions of the *dispersion of expectation values*

$$\phi(\hat{m}_N^2) - (\phi(\hat{m}_N))^2 . \tag{31}$$

Such a more general discussion would also be necessary to give a formal definition of approximate classical observables.

- One could, of course, also try to replace the maximum-entropy ensemble (for some given thermal state) by some other reasonable ensemble of pure states. One could, for example, try to minimize the dispersion of certain observables (such as the position operators of the nuclei in a molecule) instead of using the maximum-entropy principle. Minimize the dispersion of the position of the nu-

clei (in a molecule) would mean to look for an ensemble μ which minimizes the integrals

$$\int_{\text{all pure states}} \{\phi(Q_j^2) - \phi(Q_j)^2\}\mu(d\phi), \quad j = 1, 2, \cdots, M, \tag{32}$$

under the boundary condition that μ gives rise to the given thermal nonpure state D_β via eq. (17). Note that we look for the ensemble μ which minimizes the integrals in eq. (32) and not for an individual pure state ϕ minimizing $\{\phi(Q_j^2) - \phi(Q_j)^2\}$. The minimization procedure in eq. (32) would lead to a decomposition μ_{local} of D_β, different from the maximal entropy decomposition and interesting for the discussion of the Born–Oppenheimer approximation. With respect to μ_{local} the *nuclei would be localized in the best way possible*. The maximum-entropy principle has the advantage, that it can be applied without choosing particular observables such as the position operators of the nuclei.

- In *algebraic quantum mechanics* [29,30,33–36,99,117], classical observables exist only *after* the limit $N \to \infty$ of infinitely many degrees of freedom. For a large but finite number of degrees of freedom (number of spins in a magnet of number of modes of the radiation field coupled to a molecule), the system under discussion behaves always fully quantum-mechanically. This serious shortcoming is overcome in the present formalism. In particular, our formalism shows that classical observables do not arise suddenly at $N = \infty$, but arise gradually as approximate classical observables taking restricted values (e.g., $\pm m_\beta$) with higher and higher probability (as N increases).

6. Large deviations theory [11]

The aim of the present section is to show how entropies like s_{mean} in fig. 5 can be computed.

In section 5 the theory of fluctuations in statistical mechanics, the so-called large-deviations theory, was used to describe the generation of approximate classical structures. Therefore an introduction to this theory of fluctuations may be helpful. An excellent presentation is given in the original paper of Lanford [76].

To have an example at hand, let us take N molecules of equal structure, all of which are modelled as having M possible energy levels with energies $\epsilon_1, \epsilon_2, \cdots, \epsilon_M$. In this example the state space Ω_N of N molecules is taken as the Cartesian product of the N state spaces of the molecules, i.e., $\Omega_N = \{\epsilon_1, \epsilon_2, \cdots, \epsilon_M\}^N$ (without superpositions). This way of choosing Ω_N corresponds to a composition rule as in *classical mechanics*. In *quantum* mechanics, the tensor product and not the Cartesian product must be used to compose systems. Let now in this "classical" example

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[11] The mathematical parts of this section could be skipped at a first reading.

$X_j \in \{\epsilon_1, \epsilon_2, \cdots, \epsilon_M\}, j = 1, 2, \cdots, N$, denote the actual energy value of the molecule j. The number M of possible energy values remains fixed, whereas the number of molecules will be variable later on, when we study how the *fluctuations* of the specific energy

$$e := \frac{\sum_{j=1}^{N} X_j}{N} \tag{33}$$

in an ensemble *"die out" with increasing number of molecules*. The energies X_j and X_k of different molecules are assumed to be independent and identically distributed (equidistributed here for simplicity).

How is the specific energy (33) distributed (for some fixed N), and how does this distribution change with increasing number N of molecules? Note that these are precisely the questions we posed in section 5: How are the pure states distributed (see fig. 4) and how does this distribution change with an increasing number of degrees of freedom (see fig. 5).

For the present classical example the answer has been given by Cramer [42]. It is reviewed here in a simplified way: Define the "Massieu potential"

$$c(y) = \lim_{N \to \infty} \frac{1}{N} \ln \frac{1}{M^N} \sum_{\Omega_N} \exp\left\{ y \sum_{1}^{N} X_j \right\} \tag{34}$$

$$= \ln \frac{1}{M} \sum_{\Omega_1} \exp\{y X_1\}, \quad y \in \mathbf{R}. \tag{35}$$

In eq. (35) the independence and identical distribution of the energies X_j have been used. The variable y formally corresponds to (minus) the inverse temperature. In traditional thermodynamics the Legendre transform of the Massieu potential (as a function of the inverse temperature) is the entropy (as a function of the energy). Hence we denote the Legendre transform of $c = c(y)$ by s,

$$s(e) \stackrel{\text{def}}{=} \sup_{y \in \mathbf{R}} \{ye - c(y)\}, \tag{36}$$

and call it an entropy. In particular situations, it may indeed coincide with the thermodynamical entropy (apart from sign and normalization conventions). In other situations, it is a Gibbs free energy (modulo a factor β), or an $f(\alpha)$-spectrum in the multifractal formalism, or the spectrum of Lyapunov coefficients of a dynamical system [92]; it also arises in the context of the quantum-mechanical measurement problem [14]. For the present classical example, Cramer's important result [42] says something about the probabilities $P_N([e_1, e_2])$ and $P_N(]e_1, e_2[)$ of finding the specific energy (33) in some arbitrarily chosen closed or open interval,

$$\limsup_{N \to \infty} \frac{1}{N} \ln P_n([e_1, e_2]) \leqslant - \left(\inf_{e \in [e_1, e_2]} s(e) \right),$$

$$\liminf_{N \to \infty} \frac{1}{N} \ln P_N(]e_1, e_2[) \geqslant - \left(\inf_{e \in]e_1, e_2[} s(e) \right).$$ (37)

If the entropy s is continuous at e_1 and e_2, one may simply write

$$\lim_{N \to \infty} \frac{1}{N} \ln P_N([e_1, e_2]) = - \left(\inf_{e \in [e_1, e_2]} s(e) \right),$$ (38)

and similarly for the open interval. These are mathematically more precise formulations of

$$P_N[e_1, e_2] \sim \exp \left\{ -N \inf_{e \in [e_1, e_2]} s(e) \right\}.$$ (39)

The result in eq. (30) corresponds to eq. (39) and should be formulated in the same way as eq. (37) in some cases (e.g., for non-continuous entropy functions, etc.).

Eq. (39) describes how fast large deviations (i.e., deviations proportional to the particle number N) "die out" with increasing N. Incidentally, the "small" deviations, proportional to $\sqrt{N}$, survive. Their behaviour is related to the behaviour of the entropy function at its minimum. Note that the entropy function has been chosen convex here (with modifications as below), in accordance with mathematical terminology, and not concave as in thermodynamics. This is just a matter of convention.

In the present classical example, the entropy function can easily be computed. Since it is the Legendre transform of a convex Massieu potential, it is itself convex. If, for example, a convex entropy function takes its minimal value 0 at points a and b, then it takes this minimal value 0 also on the line

$$\lambda a + (1 - \lambda) b, \quad \lambda \in [0, 1].$$ (40)

This *convexity of the entropy function is nice from a mathematical point of view but unpleasant for some physical applications.*

Let us study this question for the example of a quantum-mechanical magnet in section 5. The respective entropy function in fig. 5 is non-convex. If one tried to derive it via a Legendre transform, one would end up with its convex hull: with an entropy function $\bar{s}_{\text{mean}}$ coinciding with s_{mean} for $m \leqslant - m_\beta$ and $m \geqslant + m_\beta$, but with a straight line $\bar{s}_{\text{mean}} = 0$ between $-m_\beta$ and $+m_\beta$. In other words: The hump between $-m_\beta$ and $+m_\beta$ would disappear! Try to insert this convex entropy function $\bar{s}_{\text{mean}}$ into eq. (30) and check that it says nothing about m-values between $-m_\beta$ and $+m_\beta$. In particular, *one could not conclude that pure states having zero expectation value of $\hat{m}$ die out with increasing number of degrees of freedom.* Incidentally, the same problem (without yet a solution) arises with left-sided multifractals [77], as in the case of diffusion-limited aggregation.

So *in the context of this paper* (where certain superpositions should disappear with increasing number of degrees of freedom), *it is enormously important to have a non-convex entropy function.*

In the following, this is achieved by use of the lemma of Varadhan [45,46]. The mathematical details will only be sketched, *emphasizing the* problems *arising with the particular large-deviation approach proposed in section 5 for quantum mechanics in individual setting.* Three approximations will be used, which can be improved immediately. This is not done here, since it would only complicate the computation without giving more insight into the main aspects of the problem.

Consider the Curie–Weiss model (in zero external field) with Hamiltonian

$$H_N = -\frac{J}{2N} \sum_{i,j=1}^{N} \sigma_{z,i}\sigma_{z,j} \,. \tag{41}$$

Here $\sigma_{z,j}$ are the Pauli matrices (spin $= \frac{1}{2}$) in z-direction for the particles $1, 2, \cdots, N$. The underlying phase space Ω_N consists now of *all pure states of the N-spin system*, i.e., all pure states on the N-fold tensor product of the 2×2-matrices $\mathbf{M}_2$

$$\mathbf{M}_2 \otimes \mathbf{M}_2 \otimes \cdots \otimes \mathbf{M}_2 \,. \tag{42}$$

The important point is that *the state space of the N-spin system is not just the N-fold Cartesian product of the state space for one spin* (the latter is isomorphic to the sphere, see fig. 3).

Let us first try to compute the "microcanonical" entropy function I for the distribution of the expectation values

$$\phi\left(\frac{1}{N}\sum_{j=1}^{N} \sigma_{z,j}\right), \tag{43}$$

where ϕ is an arbitrary pure state of the N-spin system. To this end, it is necessary to compute the Massieu potential

$$\lim_{N\to\infty} \frac{1}{N}\ln \int_{\Omega_N} \exp\left\{ y\phi\left(\sum_{j=1}^{N} \sigma_{z,j}\right) \right\} \mu_{\mathrm{eqp}}(d\phi) \,. \tag{44}$$

Here an approximation will be used, taking instead the Massieu potential

$$c(y) \overset{\text{def}}{=} \ln \int_{\Omega_1} \exp\{y\phi(\sigma_{z,1})\}\mu_{\mathrm{eqp}}(d\phi) \,, \tag{45}$$

which is actually an integral over the surface of the sphere S_2 and can be evaluated to give $c(y) = \ln(\sinh y/y)$. Incidentally, the corresponding Massieu-potential for the classical Curie–Weiss model is given as $\ln(\cosh y)$ [46]. The Legendre transform of $c(y) = \ln(\sinh y/y)$ will be called I, to distinguish it clearly from the "canonical"

entropy function s_{mean} below. The entropy function s_{mean} is related to the entropy function I by Varadhan's lemma.

The second approximation used here concerns the maximal-entropy ensemble of pure states compatible with the thermal density operator D_β, which is of the form given in eq. (28): Instead of computing the "Hamiltonian" $\tilde{H}_N$, the original Hamiltonian H_N in eq. (41) will be taken, ending up in the ensemble

$$\frac{\exp\{-\beta\phi(H_N)\}\mu_{eqp}}{\int_{\Omega_N}\exp\{-\beta\phi(H_N)\}\mu_{eqp}(d\phi)} \ . \tag{46}$$

Note that $-\beta H_N$ can be expressed as a function

$$-\beta H_N = Nh_\beta(\hat{m}) \tag{47}$$

of the mean magnetization operator

$$\hat{m} = \frac{1}{N}\sum_{j=1}^{N}\sigma_{z,j} , \tag{48}$$

where

$$h_\beta(x) \stackrel{\text{def}}{=} \tfrac{1}{2}\beta Jx^2 . \tag{49}$$

The second approximation (46) is reasonable, since the mean magnetization operator $\hat{m}$ is "almost" commuting with all other observables for large N.

Now comes the third and last approximation, replacing

$$-\beta\phi(H_N) = N\phi(h_\beta(\hat{m})) \tag{50}$$

by $Nh_\beta(\phi(\hat{m}))$. This third approximation allows to rewrite the ensemble in eq. (46) as

$$\frac{\exp\{Nh_\beta(\phi(\hat{m}))\}\ \mu_{eqp}}{\int_{\Omega_N}\exp\{Nh_\beta(\phi(\hat{m}))\}\ \mu_{eqp}(d\phi)} \ . \tag{51}$$

At this stage the entropy function s^β_{mean} for the distributions $P_{\beta,N}$ of the expectation values $\phi(\hat{m})$ (see eq. (30)) with respect to the ensembles in eq. (51) can be computed. By *Varadhan's lemma* [46] the entropy function s^β_{mean} is given as

$$s^\beta_{mean}(m) = \{I(m) - h_\beta(m)\} - \inf_{m\in\mathbf{R}}\{I(m) - h_\beta(m)\} , \tag{52}$$

where I is the Legendre transform of the Massieu-potential

$$c(y) = \ln\left(\frac{\sinh y}{y}\right) , \quad y\in\mathbf{R} , \tag{53}$$

defined in eq. (45). Figure 5 is based on this result, where the temperature has been taken as one third of the critical (Curie) temperature.

Consider now the limit $N \to \infty$. In algebraic quantum mechanics, this limit gives rise to a strictly classical observable "magnetization", i.e., the operator

$$\hat{m}_\infty \overset{\text{def}}{=} \sigma - \underset{N \to \infty}{\text{weak lim}} \frac{1}{N} \sum_{j=1}^{N} \sigma_{z,j} \qquad (54)$$

(in the GNS-representation [34] with respect to a thermal limit state) *commutes* with all the operators in the quasilocal C*-algebra (generated by the spin operators). The thermal limit state can be shown to be a direct sum (or direct integral) of disjoint factor KMS-states [29,30] having a dispersion-free expectation value of any classical observable. Therefore the mean magnetization $\hat{m}_\infty$, in particular, takes dispersion-free expectation values with respect to the factor KMS-states.

The individual setting of quantum mechanics gives the possibility to introduce approximate classical observables. The superposition principle is still fully valid for finite N, but nevertheless pure states with zero expectation value of $\hat{m}_N$ "die out" with increasing N. Pure states ϕ "survive in the limit $N \to \infty$" only if the respective expectation values $\phi(\hat{m}_N)$ converge to the expectation values of $\hat{m}_\infty$ with respect to factor KMS-states. This last claim is not yet proven in every detail. One must compute the distribution of the dispersion $\phi(\hat{m}_N^2) - \phi(\hat{m}_N)^2$ for pure states in the maximum entropy decomposition, which is currently under investigation. This would also give more detailed insight into the concept of an approximate classical observable. I expect that the distribution of the dispersion $\phi(\hat{m}_N^2) - \phi(\hat{m}_N)^2$ "dies out" with increasing N and that this process can again be described by an appropriate entropy $s_{\text{dispersion}}^\beta$ (analogous to s_{mean}^β, but with only one minimum even below the Curie temperature).

7. A heuristic dynamical derivation of the maximum-entropy principle

It might be worthwhile to summarize a little bit: The thermal state D_β is introduced in statistical quantum mechanics as a state which is stable under perturbations [33]. Here we went further insofar as we looked for stable decompositions of the thermal state into pure states. The maximum-entropy decomposition of D_β, in particular, leads to a unique ensemble μ_{max} of pure states with maximum entropy. This ensemble μ_{max} is not concentrated on eigenstates, i.e., the pure states in the ensemble can be nonstationary. The reason for using a maximal entropy ensemble was to get a stable description under "external perturbations". In particular, not only the Hamiltonian of the system under consideration gives rise to a dynamics, but also the external influences of the "environment". It would be nice to understand this dynamics in a better way and to "derive" the maximum-entropy principle from dynamical considerations. Though the maximum-entropy decomposition is favored here, it would be very interesting to know something about its relation to

other decompositions: The decomposition of a molecular thermal state into pure (non-stationary) *best-localized* states, for example, as introduced in eq. (32).

Let us start with the von Neumann point of view (see section 4) of a molecule coupled to the radiation field (with an additional electromagnetic input coming from the experimenter). The situation is sketched in fig. 6: Starting from an arbitrary fixed initial state, one will end up with eigenstates of the coupling operator between molecule and field (the dipole operator). In fig. 6 these eigenstates of the coupling operator are identified with the poles of the sphere. According to the projection postulate, the probability to reach the north pole is $\frac{1}{2}(1 + \cos\{\vartheta\})$ and the probability to reach the south pole is $\frac{1}{2}(1 - \cos\{\vartheta\})$, where ϑ (and φ) are the spherical coordinates of the initial state.

In von Neumann's point of view, quantum jumps are replaced by a stochastic dynamics [13,14,28,57–59,100,101,150]: Depending on the state of the "environment" (e.g., the radiation or gravitation field or a measurement apparatus), the initial state of the two-level molecule is either transformed into a spin-up or into a spin-down state. Stochasticity comes in because the state of the environment (which is a system with many degrees of freedom) cannot be determined.

In statistical quantum mechanics, the process during spectroscopic measurement is described by some density operator dynamics, such as that one determined by the Karplus–Schwinger equation (4). One might try now to find a stochastic dynamics on the level of pure states which corresponds to the original density-operator dynamics via eqs. (3), (17). In other words: Starting from some initial
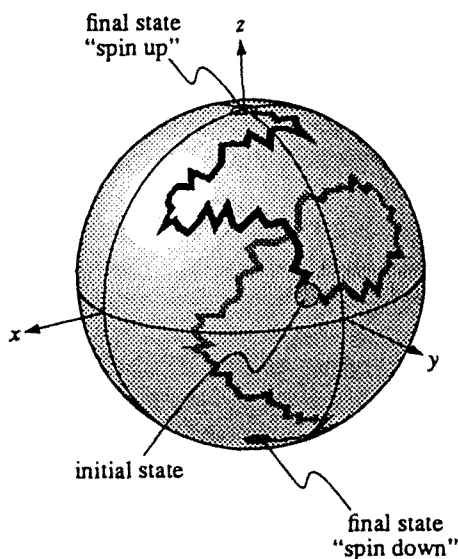

Fig. 6. Sketch of a stochastic dynamics for pure states of a two-level molecule, based on the von Neumann point of view (see section 4): Starting from an arbitrary initial state one ends up with eigenstates of the dipole moment operator (coupling the two-level molecule to the radiation field).

state (or some initial ensemble μ_0 of pure states) one would get ensembles μ_t (of pure states) at time t, finally ending up with some asymptotic ensemble μ_∞ in the limit $t \to \infty$.

The difficulty is that non-pure states cannot be uniquely decomposed into pure states (see section 2). Hence completely different stochastic dynamics on the level of pure states may (and are indeed) compatible with one and the same density operator dynamics [136]. Therefore it is necessary to derive a stochastic (nonlinear) dynamics on the pure-state level from first principles, without simply relying on density operator dynamics. Here this will not be discussed in detail. *Keywords would be: Hartree approximation and dressing procedures.*

The important point is: Stochastic dynamics on the pure-state level can be "derived" [13,14,28,57–59,100,101,150] [12]. Let us hence *assume that the "external perturbations" coming from the environment are modelled by a stochastic dynamics on the pure states of the system under consideration*, e.g., a quantum-mechanical magnet or a molecule coupled to the radiation field (or some other environment such as a matrix in which it is embedded). One will, of course, usually not deal with such a simple pure state space as the surface of a sphere in fig. 6. Let us furthermore assume that the asymptotic ensemble μ_∞ of the stochastic dynamics considered fulfills a *detailed-balance condition*:

$$R(\Gamma_1 \to \Gamma_2)\mu_\infty(\Gamma_1) = R(\Gamma_2 \to \Gamma_1)\mu_\infty(\Gamma_2) . \tag{55}$$

Here $R(\Gamma_a \to \Gamma_b)$ is the transition rate between two arbitrary (Borel) sets of pure states; think of two subsets of the surface S_2 of the sphere, which is the simplest space of pure states (see fig. 3). This sort of detailed balance condition has, for example, been used by Einstein in his derivation of the spontaneous decay rates for (eigenstates) of a molecule in contact with the radiation field. The situation considered here is actually quite similar to that one considered by Einstein, with the only difference that we accept arbitrary pure states instead of eigenstates of the Hamiltonian.

Let us therefore assume to have modelled the "external perturbations" of a system by a stochastic dynamics on the level of pure states (of this system), fulfilling the detailed-balance condition (55). *Then it can be shown that the relative entropy*

$$S(\mu_t \mid \mu_\infty) \overset{\text{def}}{=} - \int_{\text{all pure states}} g_t \ln g_t \, d\mu_\infty \tag{56}$$

of the ensembles μ_t (of pure states) at time t with respect to the asymptotic ensemble

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[12] Actually, derivation is difficult and the existing examples have been invented to get some idea how derived dynamics could look like. Nevertheless, enormous progress has been made in the last years. Incidentally, the contributions of V. Belavkin (Nottingham) to stochastic quantum dynamics should most certainly be mentioned. Unfortunately, I do not (yet) understand them well enough to be allowed to cite them. An interesting discussion with Prof. Belavkin is gratefully acknowledged.

μ_∞ *of the stochastic dynamics increases.* Here $\mu_t = g_t \mu_\infty$ has been written as {function g_t on the space of pure states × asymptotic ensemble μ_∞}. If μ_t does not have this structure, then its relative entropy with respect to μ_∞ is $-\infty$, and the relative entropy can again only increase.

The relative entropy of eq. (56) corresponds to the absolute entropy in eq. (27) used for the maximum-entropy principle. Comparing (in a hand-waving argument) relative and absolute entropy, one can "show" that the absolute entropy of the ensembles μ_t increases, *if* the "energy" of the system under consideration does not change. Hence one may expect that coupling to an environment leads to an increase of the absolute entropy (27) of the ensemble of pure states, and hence finally to an ensemble of maximum entropy. *In short: Starting with some arbitrary decomposition of a thermal state D_β, the coupling to the environment will (via a stochastic dynamics on the pure states) lead to a maximum-entropy decomposition.*

8. Transition probabilities and lifetimes

In this section, it will be shown how stochastic dynamics on the pure-state space of a system can in principle be discussed, and *how transition probabilities and lifetimes* can be computed. In this section, transition probabilities do not refer to transitions between eigenstates of the Hamiltonian, but to transitions between arbitrary regions of the pure-state space (e.g., starting from an arbitrary pure initial state to an arbitrary part of the surface of the sphere, in case of a twolevel system, see fig. 6). The system in question could, e.g., be a magnet or a molecule. This system is thought to be perturbed from "outside", i.e., its dynamics also depends on the (pure) state ω of the environment. Hence the state ω becomes the stochastic variable in the description of the system.

Remark

In this context, not only the system but also its *environment is assumed to be in a pure state*, though this pure state is perhaps not known and can only be estimated. Initially, the statistical non-pure state of the environment will, for example, be described by a thermal density operator D_β. The respective maximum-entropy ensemble $\mu_{\text{max,envir}}$ of pure states (now taken for a particular *environment* such as a measurement device, and not for the original system) then describes the probability to find the environment in some pure state ω. Depending on ω, the state ϕ of the original system will develop dynamically in a different way. The result is a stochastic dynamics on the pure states ϕ of the system (see fig. 6).

In fig. 7, for example, the situation of a mean-field magnet is taken up again (see fig. 5) with its characteristic entropy function s_{mean} computed in section 6. How could a dynamical description look like, where the dynamics does not only stem from the mean-field Hamiltonian (41) of the magnet alone, but also from
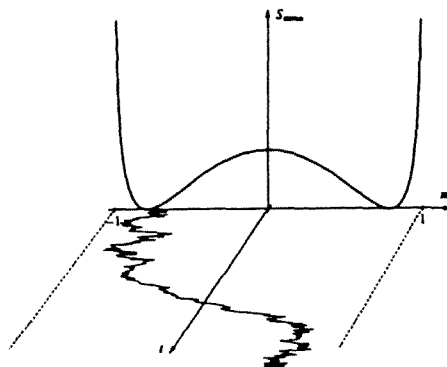
Fig. 7. Here the situation of fig. 5 with its characteristic entropy function s_{mean} is shown again together with a possible dynamical evolution of the magnetization m of an individual pure state. The magnet is thought to consist of a fixed finite number N of spins at a fixed temperature. The dynamics is sketched and not based on some computation.

external stochastic perturbations (e.g., an external fluctuating magnetic field). This additional stochastic dynamics prevents, in particular, that eigenstates of the Hamiltonian (41) are stable as they would be in an isolated description. Consider a given initial state ϕ_0, with, say, expectation value $-m_\beta$ of the specific magnetization $\hat{m}$. Since most pure states in the maximum entropy ensemble (decomposing the thermal non-pure state D_β) have magnetization expectation value $+m_\beta$ or $-m_\beta$, and since the maximum-entropy ensemble describes the situation in thermal equilibrium, one may expect that the dynamical evolution

$$t \mapsto \phi_t(\hat{m}) \tag{57}$$

with initial value $-m_\beta$ will remain near $-m_\beta$ for quite some time, but nevertheless be able to change to the other side with values near $+m_\beta$ (see fig. 7), as long as the number N of spins is finite. This will be the more the case, the more the temperature is raised to the Curie point, at which the entropy s_{mean} gets very flat and changes from a double- into a one-minimum shape above $T_{crit.}$.

Or have a look at fig. 6, where a simple two-level system is taken as an example. *Starting with some arbitrary initial state, one could, for example, be interested to know if the dynamics leads to the north- or to the south pole, i.e., if the dynamics leads to the spin-up or the spin-down eigenstate of the dipole operator (which couples molecule and field). Or one could be interested in the time necessary to get the north- or south pole ("how long does it take for some arbitrary initial state to become an eigenstate of the dipole-moment operator in a spectroscopic process?").* A realistic situation could, of course, be much more complex. Also, given the philosophy of the present paper, eigenstates would not play a predominant role (neither eigenstates of the Hamiltonian nor eigenstates of the dipole moment operator). It would, in particular, be *interesting to compute lifetimes of the ground state of a chiral molecule (see section 1), i.e., how long it does take for the proper ground state of a chiral mole-*

cule to decay into the handed states. Here, for the sake of simplicity, the von Neumann point of view is taken and the "semi-realistic" example below is chosen accordingly.

We shall, in the following, stick to the situation of fig. 6. Starting from some initial state, we deal with trajectories depending on the state ω of the environment (which arise with a certain probability P, i.e., P is a probability measure on the pure-state space of the environment). These trajectories are trajectories in the state space, and not trajectories in the sense of (p, q) values varying with time (see fig. 6). The pure state ϕ_t depends on the state ω of the environment

$$\phi_t = \phi_t(\omega) \, . \tag{58}$$

This nomenclature could be misleading for a mathematician. It should simply indicate that ϕ_t depends on an additional variable ω. If one chooses a fixed initial state ϕ_0 for the system (as in fig. 6), one has

$$\phi_0(\omega) = \phi_0 \tag{59}$$

for all pure states ω of the environment. Let us now draw little circles around the north- and south poles, respectively, and ask when and where a particular trajectory ω passes these circles [13] (little circles are used, since an actual trajectory will usually not reach a pole precisely). The respective time will be denoted by $\tau(\omega)$ and called a *stopping time* [127]. Some of the trajectories will first pass the circle near the north pole, and some of the trajectories will first pass the circle near the south pole (*here*, we are not interested in what happens later on, though that would be very interesting to discuss). It will be tried below to compute the transition probabilities, i.e., the probabilities to pass first the circle near the north- or the south pole, respectively.

Only a very simple example will be discussed, the technique being applicable to any stochastic dynamics on the pure-state space [14]. The example is given by the following class of (Stratonovich) stochastic differential equations

$$d\vartheta_t = -2\kappa \sin(\vartheta_t) \cos(\vartheta_t) \, dt + 2\nu \sin(\vartheta_t) \circ dW_t \, , \tag{60}$$

with κ and ν being fixed positive constants. Here ϑ is one of the spherical coordinates (for simplicity, it is assumed that the problem does not depend on the azimutal angle φ), and W_t is a one-dimensional Wiener process [19,127]. More general stochastic dynamics could be formulated (adding, e.g., the experimenter's input to the drift term $-2\kappa \sin(\vartheta_t) \cos(\vartheta_t) \, dt$). Actually, all the variables also depend on the stochastic variable ω, which describes the state of the environment ($\equiv$ the path of the Wiener process in the mathematical description). Hence, eq. (60) could also be written as

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[13] Pure states of the environment and state- trajectories of the system are in one-one correspondence and hence denoted by the same variable ω.

[14] This last part of the section could be skipped at a first reading.

$$d\vartheta_t(\omega) = -2\kappa \sin\{\vartheta_t(\omega)\} \cos\{\vartheta_t(\omega)\} \, dt + 2\nu \sin\{\vartheta_t(\omega)\} \circ dW_t(\omega) . \tag{61}$$

An equivalent integral version of eq. (61) is

$$\vartheta_t(\omega) = \vartheta_0 + \int_0^t (-2\kappa) \sin\{\vartheta_s(\omega)\} \cos\{\vartheta_s(\omega)\} \, ds$$

$$+ \int_0^t 2\nu \sin\{\vartheta_s(\omega)\} \circ dW_s(\omega) . \tag{62}$$

Roughly spoken, these integrals are computed for every path ω. The "difficult" integral is the second one (with the Wiener process W_t), which for a *Stratonovich* stochastic differential equation is defined as the limit

$$\lim_{\delta \to 0} 2\nu \sum_{k=1}^{K} \frac{\sin\{\vartheta_{s_k}(\omega)\} + \sin\{\vartheta_{s_{k+1}}(\omega)\}}{2} (W_{s_{k+1}}(\omega) - W_{s_k}(\omega)) , \tag{63}$$

where s_k, $k = 1, 2, 3, \cdots, K$, is a partition of the interval $[0, t]$ with a maximal distance δ between the partition points [19]. In an *Itô* stochastic differential equation [19], on the other hand, this integral would be defined as

$$\lim_{\delta \to 0} 2\nu \sum_{k=1}^{K} \sin\{\vartheta_{s_k}(\omega)\}(W_{s_{k+1}}(\omega) - W_{s_k}(\omega)) . \tag{64}$$

It is important to realize that the definitions in eqs. (63, 64) give rise to different results (since the Wiener paths are not regular enough). *Physical* reasoning leads to *Stratonovich* stochastic differential equation, which can be reformulated as an *Itô* equation with different drift term [19]. The Stratonovich equation (60), for example, corresponds to the Itô equation

$$d\vartheta_t = \left\{ -2\kappa \sin(\vartheta_t) \cos(\vartheta_t) + 2\nu^2 \frac{\partial \sin(\vartheta_t)}{\partial \vartheta} \sin(\vartheta_t) \right\} dt + 2\nu \sin(\vartheta_t) \, dW_t . \tag{65}$$

Reformulation as *Itô* equation has mathematical advantages: An *Itô* integral (as in eq. (64)), depending on t, is a martingale [15], whereas the corresponding *Stratonovich* integral is not.

For the particular values $\kappa = \nu = \frac{1}{2}$, the stochastic process (60) is the Gisin process [59], which has the correct transition probabilities $\frac{1}{2}(1 \pm \cos \vartheta)$ for transitions to the poles, i.e., reproduces the transition probabilities of the *projection postulate*. Hence the class (60) of stochastic dynamics is not entirely artificial. Note that the transition probabilities discussed here are not transition probabilities between eigenstates of the Hamiltonian, but probabilities for an arbitrary pure initial state to get to some chosen region of the pure-state space (some region on the surface of the sphere in case of a two-level system).

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[15] Here martingales are always taken with respect to the time t and not with respect to particle number N.

Incidentally, the equation (60) can be transformed by introducing a new variable $x_t := -\log\tan(\frac{1}{2}\vartheta_t)$ into

$$dx_t = 2\kappa \tanh(x_t)\, dt - 2\nu\, dW_t, \tag{66}$$

which will be used for the mathematical discussion below (the heuristic physical discussion will still be lead in terms of fig. 6). Note that for this stochastic integral equation the Stratonovich and Itô versions coincide (since the diffusion term does only contain the Wiener differential dW_s, but not contain a function of W_s or a function of the solution x_s of the stochastic equation). The mentioned transformation changes the domain of definition from $0 \leqslant \vartheta \leqslant \pi$ to $-\infty \leqslant x \leqslant +\infty$. Hence small circles around north- and south pole do now correspond to scalars x_- and x_+, where x_- is very negative ("near" $-\infty$) and x_+ is very positive ("near" $+\infty$). The initial value of the trajectories considered (corresponding to the initial state on the sphere S_2) will be denoted by x_0.

Consider again the stopping time $\tau(\omega)$ introduced above. At time $\tau(\omega)$, the trajectory

$$t \mapsto x_t(\omega) \tag{67}$$

with initial value x_0 reaches either x_- or x_+, i.e.,

$$x_{\tau(\omega)}(\omega) = x_- \quad \text{or} \quad x_{\tau(\omega)}(\omega) = x_+. \tag{68}$$

Assume now that there exists a function

$$h : \mathbf{R} \to \mathbf{R} \tag{69}$$

such that

$$h(x_t) = h(x_t(\omega)), \quad t \in \mathbf{R}, \tag{70}$$

is a *martingale*. Recall that a martingale

$$t \to Z_t,$$

$$Z_t = Z_t(\omega), \tag{71}$$

is a *typical stochastic process in the usual sense*, i.e., given the values $Z_{s_1}(\omega)$ for some time s_1, the best prediction for Z_{s_2}, $s_2 > s_1$ is Z_{s_1} itself. A Wiener process, for example, is a martingale. For a martingale $h(x_t)$, Doob's optional stopping theorem [127] implies that

$$h(x_0) = \int_{\text{states of the environment}} h(x_{\tau(\omega)}(\omega))\, dP(\omega) \tag{72}$$

$$= h(x_-)P\{\omega | x_{\tau(\omega)}(\omega) = x_-\} + h(x_+)P\{\omega | x_{\tau(\omega)}(\omega) = x_+\}. \tag{73}$$

The equality in eq. (73) is an immediate consequence of eq. (68), with $P\{\omega | x_{\tau(\omega)}(\omega) = x_-\}$ and $P\{\omega | x_{\tau(\omega)}(\omega) = x_+\}$ being the transition probabilities to

(small circles around) the south- and the north pole, respectively, which sum up to one,

$$P\{\omega|x_{\tau(\omega)}(\omega) = x_-\} + P\{\omega|x_{\tau(\omega)}(\omega) = x_+\} = 1 \,. \tag{74}$$

Denoting these transition probabilities by P_- and P_+, one arrives at the simple result

$$P_+ = \frac{h(x_-) - h(x_0)}{h(x_-) - h(x_+)} \,, \tag{75}$$

$$P_- = \frac{h(x_0) - h(x_+)}{h(x_-) - h(x_+)} \,. \tag{76}$$

Therefore, slightly generalizing, *if one has a real-valued function h on the pure-state space such that* $h(\phi_t) = h(\phi_t(\omega))$ [16] *is a martingale* (where ϕ is an element of the pure-state space), eqs. (75), (76) allow to compute the transition probabilities looked for. If the pure-state space is, for example, the surface S_2 of the 3-sphere (as in fig. 3), one would have to find an appropriate function

$$h : S_2 \to \mathbf{R} \tag{77}$$

such that

$$h(\phi_t) = h(\phi_t(\omega)) \tag{78}$$

is a martingale. For the computation of transition probabilities, the function h has to be chosen in such a way that it is constant on the little circles around north- and south-pole (or conversely, these little "circles" have to be replaced by little curves around the poles, on which the function h is constant).

Hence the problem is finally to *find appropriate real-valued functions h on the pure-state space such that* $h(\phi_t) = h(\phi_t(\omega))$ *is a martingale.* Martingales are time-conserved quantities in the sense of eqs. (115), (116), or integrals of motion, which has already been used in eq. (72). *In the individual formalism of quantum mechanics (with a stochastic dynamics on the pure-state space) martingales replace the usual "integrals of motion" such as, e.g., the energy or the angular momentum.* Hence, for a complete description of the quantum processes arising during a spectroscopic investigation, one would need not only a stochastic dynamics (on the pure states) but also enough martingales to get a clear impression of the stochastic process and as a means for the computation of transition probabilities.

Martingales can be found using Itô's change-of-variable formula (see Appendix 2). Consider our example of a stochastic differential equation (eq. (66)),

$$dx_t = 2\kappa \tanh(x_t) \, dt - 2\nu \, dW_t \,. \tag{79}$$

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[16] This notation should only indicate that ϕ_t and $h(\phi_t)$ are functions of the state ω of the environment.

Then by Itô's formula (125), any differentiable function $h: \mathbf{R} \to \mathbf{R}$ fulfills

$$h(x_t) - h(x_0)$$

$$= \int_0^t h'(x_s)\{2\kappa \tanh(x_s)\, ds - 2\nu\, dW_s\} + \frac{1}{2}\int_0^t h''(x_s)4\nu^2\, ds$$

$$= \int_0^t \{2\kappa \tanh(x_s)\, h'(x_s) + 2\nu^2 h''(x_s)\} + \int_0^t (-2\nu)h'(x_s)\, dW_s. \tag{80}$$

Since

$$\int_0^t (-2\nu)h'(x_s)\, dW_s \tag{81}$$

is a martingale, it is clear that the $h(x_t) = h(x_t(\omega))$ is a martingale *if*

$$h''(x) + \frac{\kappa}{\nu^2}\tanh(x)\, h'(x) = 0, \quad x \in \mathbf{R}, \tag{82}$$

holds. Therefore the function

$$h(x) = \int_0^x \exp\left\{\int_0^y -\frac{\kappa}{\nu^2}\tanh(z)dz\right\} dy \tag{83}$$

$$= \int_0^x (\cosh y)^{-\kappa/\nu^2}\, dy \tag{84}$$

is a solution leading to a martingale $h(x_t) = h(x_t(\omega))$. In the case of the Gisin process (with $\kappa = \nu = \frac{1}{2}$) one arrives at

$$h(x) = \tanh x, \tag{85}$$

and therefore gets transition probabilities (see eqs. (75), (76))

$$P_+ = \frac{\tanh(x_-) - \tanh(x_0)}{\tanh(x_-) - \tanh(x_+)}, \tag{86}$$

$$P_- = \frac{\tanh(x_0) - \tanh(x_+)}{\tanh(x_-) - \tanh(x_+)}. \tag{87}$$

Since the function tanh converges quickly to ± 1 for $x \to \pm\infty$, these transition probabilities (to reach small circles around the poles) converge quickly to

$$\frac{1 \pm \tanh x_0}{2} = \frac{1 \pm \cos\vartheta}{2} \tag{88}$$

and hence reproduce the projection postulate. This is not the case for other values of κ/ν^2. For $\kappa/\nu^2 = 4$, e.g., one arrives at

$$h(x) = -\frac{1}{3}\tanh^3 x + \tanh x, \tag{89}$$

which gives rise to transition probabilities

$$\frac{2 \pm 3 \cos \vartheta \mp \cos^3 \vartheta}{4} , \tag{90}$$

differing from the "correct" transition probabilities in eq. (88) up to 10% (depending on the initial state).

To get results about the *time necessary for a transition* , similar techniques can be applied. One may, for example, consider functions $h : \mathbf{R}^2 \to \mathbf{R}$ such that

$$h(x_t, [x, x]_t) = h(x_t(\omega), [x, x]_t(\omega)) \tag{91}$$

is a martingale (where $[x, x]$ is the Doob–Meyer bracket, introduced in Appendix 2).

The main problem with this and other, more involved, computations is that one needs numerical capacity to solve (usual, i.e., *non*-stochastic) partial differential equations.

Summarizing: It is desirable to have a dynamical theory on the level of pure states, not only encorporating the Hamiltonian dynamics of the system considered, but encorporating also external stochastic perturbations. The maximum-entropy ensemble (corresponding to a thermal non-pure state D_β) can be explained by such dynamical considerations. Transition probabilities and transition times can be computed using martingale theory (and numerical procedures to solve partial differential equations). Martingales are conserved quantities, replacing the usual conserved quantities such as energy, angular momentum, etc. Given such a dynamical approach on the pure-state level, interesting questions to solve would be:

• How long does it take for the symmetric ground state of a chiral molecule to decay into left- and right-handed (or other) states?

• Can one distinguish between the Bohr–Einstein and the von Neumann point of view, respectively? Can one find certain situations (e.g., large level splitting), such that at least one of them is "correct?"

9. The structure of single molecules

Let us again consider our previous example, namely an ammonia-type molecule, or the joint system {ammonia-type molecule & radiation field}, or the joint system of an ammonia-type molecule with another type of environment. We are interested in thermal equilibrium states, and try to explain the kind of phase transition alluded to in table 1.

Let us first recall the prescription given by the *standard formalism* of quantum statistical mechanics [33,117]. This prescription would read as follows: "Try to construct different thermal states with different expectation values of an order parameter." Various reasons can be given to show that this prescription cannot work for

our problem (where the order parameter can be thought to be the coordinate of the inversion oscillation):

- *If* the prescription worked, then one would end up with chiral *strictly stationary* thermal states with density operators $D_{\beta,L}$ and $D_{\beta,R}$. No racemization would take place, contrary to experimental experience.

- For *finitely* many modes of the field, the prescription does *never* lead to different order parameters (say for left- and right-handed thermal states). Considering, in particular, an isolated molecule (which consists of finitely many particles and therefore has only finitely many degrees of freedom), the prescription does not work. *Reason*: for *finitely* many degrees of freedom there exists *exactly one* thermal non-pure state (β-KMS state [33]) for every inverse temperature β, namely that one with density operator D_β. This argument is similar to the result in eq. (24) in the discussion of the Born–Oppenheimer approximation. Note that the uniqueness of the thermal state is independent of symmetry considerations (i.e., is also true if the weak neutral current terms are taken into account).

- In the statistical approach, one tries to perturb the symmetry of the Hamiltonian by some small "external" influence, such as an external magnetic field B, and considers the zero-field limit of the density operators

$$D_{\beta,\text{pos}} \overset{\text{def}}{=} \lim_{B \to +0} D_{\beta,B} \,, \tag{92}$$

$$D_{\beta,\text{neg}} \overset{\text{def}}{=} \lim_{B \to -0} D_{\beta,B} \,. \tag{93}$$

If the two density operators $D_{\beta,\text{pos.}}$ and $D_{\beta,\text{neg.}}$ do not coincide [17], one has constructed the two different thermal non-pure states looked for. Unfortunately, for *finitely* many degrees of freedom, this "trick" does *not* work, i.e., leads to identical and not to different results for $D_{\beta,\text{pos.}}$ and $D_{\beta,\text{neg.}}$.

- For *infinitely* many degrees of freedom, e.g., with consideration of all modes of the radiation field, different thermal states (with identical inverse temperature) can exist [33]. But *Araki perturbation theory* [33] shows that a change of the level splitting (as in table 1) does *not* lead to a phase transition. Either one has handed thermal states for *all* ammonia-type molecules or one has no handed thermal states for *all* ammonia-type molecules [5,49–52]. Araki perturbation theory for thermal states is mathematically rigorous, in contrary to usual perturbation theory as it is used for pure eigenstates of a Hamiltonian. Incidentally, for ground states (i.e., for temperature zero) the situation is differ-

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[17] Density operators are used here, even if this is slightly incorrect. One should formulate everything in terms of non-pure states.

ent [6–8,95,123,124]. These interesting matters are not discussed in the present
paper.

- Even if the prescription would work for infinitely many degrees of freedom,
  one would at least expect that it works for a *large but finite* number of degrees of
  freedom, too. This is not the case. In algebraic quantum mechanics, superselec-
  tion rules are equivalent to classical observables and arise *after* the limit
  $N \to \infty$ of particle number going to infinity. For finite N, the superposition
  principle is fully valid.

- Statistical quantum mechanics could also be used to exclude the Born–Oppen-
  heimer description or to deny the existence of isomeric molecular species. Con-
  sider, e.g., different isomeric molecules. These isomeric molecules are
  described by the same Hamiltonian (since the latter depends only on the num-
  ber of electrons and the charges of the nuclei). Hence the isomeric molecules
  have the same thermal state (because the thermal state is determined by the Ha-
  miltonian). This unique thermal state gives unique expectation values for the
  position operators of the nuclei, and even zero expectation values as in eq. (24)
  if the Hamiltonian is symmetric under space inversion. From a physical or
  chemical point of view, this line of arguments, though formally correct, gives
  rise to strange results, since it excludes nuclear frame, chirality and isomeric
  molecular species as well as all other approximate classical structures.

*Therefore the usual statistical formalism of quantum mechanics as codified in alge-
braic quantum mechanics [69,96,99,117,126] does not lead to classical structures
and phase transitions for systems with finitely many degrees of freedom.*

Remark
Nevertheless, classical observables can be introduced in algebraic quantum
mechanics by group-theoretical methods [2,3] without ever thinking about the
number of degrees of freedom. It is an enormous achievment of algebraic quantum
mechanics that both-classical and quantum mechanics-can be treated by one and
the same formalism. Algebraic quantum mechanics is also helpful (in a mathemati-
cal sense) for the individual setting of quantum mechanics as developed in the pres-
ent paper. *The critique here refers to the construction of classical observables by
limits.* Incidentally, in W*-algebraic quantum mechanics thermal limit situations
are usually described by type III-W*-algebras [33]. But pure states on type-III W*-
algebras do not even fulfill the Jauch–Piron condition [4,37,64] and hence are very
pathological. Therefore the respective thermal state ($\equiv \beta$-KMS state) should not
be decomposed into pure states at all. If one wants to decompose the thermic state
into pure states (in a situation with infinitely many degrees of freedom), one must
use a C*-algebraic theory. For such a C*-algebraic theory of thermal states (of sys-
tems with infinitely many degrees of freedom) one could try to understand limits
$N \to \infty$. On the level of *ensembles of pure states* such a limit makes sense if the max-

imum-entropy ensembles are used. It does usually not make sense if the decomposition into eigenstates of the Hamiltonian is used.

Looking at ammonia-type molecules, the main problem in usual statistical quantum theory is again that a thermal non-pure state D_β cannot be uniquely decomposed into pure states (see section 2). One and the same thermal state D_β can be decomposed differently into pure states, such that the distribution of the inversion coordinate q is, e.g., centered around $q = 0$ or, this is another possibility, is centered around two different values $\pm q_\beta$. These two possibilities are sketched in fig. 8. The second one (with two maxima) refers to a situation with an approximate classical structure (where, of course, also the dynamics has to be taken into account, see section 10). A decomposition of D_β into symmetry-adapted eigenstates (of the Hamiltonian) would lead to a δ-distribution p concentrated at $q = 0$. Since, in statistical quantum mechanics, all these different decompositions are considered as equivalent, no approximate classical structures can be introduced.

Incidentally, the same problem arises with isomeric molecular species. Having the same thermal non-pure state D_β, one can consider decompositions leading indeed to different isomeric species (illustrated on the right part of fig. 8), or decompositions into eigenstates (which are superpositions of the two potential isomeric species, see left part of fig. 8 and eq. (24)).

Let us now pass in review the *approach advocated in the present paper*. It has been argued that the robust thermal state D_β should be decomposed in such a ("robust") way into pure states that the resulting ensemble has *maximum entropy with respect to equipartition of pure states*. Hence from the very beginning, the resulting ensemble of pure states is uniquely determined. As shown in section 6, such a maximum-entropy ensemble has a tendency to be concentrated on different parts of the pure-state space (because that increases the entropy defined in eq. (27)). Correspondingly, the expectation values of molecular coordinates (an inversion coordinate q, for example), can be concentrated on different values of q (e.g., two values $\pm q_\beta$, see fig. 8). For the sequence *monodeuteroanilin $\to$ ammonia $\to \cdots \to$ aspartic acid* of molecular species, one expects to get distributions of the inversion coordinate q, which are first concentrated around $q = 0$ (for monodeuteroanlinin and ammonia), but develop two concentration points $\pm q_\beta$ for prop-

Fig. 8. Different distributions p of the inversion coordinate q in an ammoniatype molecule, referring to different decompositions of the same thermal nonpure state into pure states. This figure refers to some fixed inverse temperature. The figure corresponds to fig. 4 and is not based on a calculation. For chiral molecules, the value $p(q = 0)$ is expected to be very low.

erly chiral molecules, such that for smaller level splitting one gets a better concentration (finally ending up with two δ-peaks).

Remark

If this heuristic idea is correct, one can introduce an entropy $s_{\text{level splitting}}$ (in analogy to the entropy s_{mean} for a strict classical observable as the magnetization), describing how fast superpositions of left- and right-handed states "die out" with decreasing level splitting of the molecular species (see table 1).

Hence in the approach of this paper, there is no principal difficulty to get *approximate classical observables and structures as well as approximate symmetry reduction already for* finitely *many degrees of freedom*. Here "symmetry-reduction" means that the symmetry of the pure states in the maximum-entropy ensemble is lower than the symmetry of the non-pure thermal state D_β. If, for example, the thermal non-pure state describes a racemate, then the maximum-entropy decomposition consists mainly of left- and right-handed states and not of their superpositions. Nevertheless, the superposition principle is still fully valid. Superpositions of left- and right-handed states exist, but may be unstable under external perturbations.

The pure states in a maximum-entropy ensemble (corresponding to some thermal non-pure state) are usually non-stationary. That is perfectly ok.: If one considers a pot of water described by a thermal non-pure state, then everybody wants the actual pure state of the water to be nonstationary, because "the water molecules in the pot move." Correspondingly, for molecules one cannot expect that only stationary states (eigenstates of the Hamiltonian) play a role. It would, for example, be interesting to know how the states of ammonia are distributed in a maximal entropy ensemble of pure states (for a given temperature). In microwave spectroscopy of ammonia, for example, different heuristic ideas are used: sometimes the problem is treated quantum-mechanically on the basis of eigenstates, and sometimes more classically (in the sense of a back and forth tunneling state / an inverting pyramid).

Obviously, it is quite difficult to work out this individual setting of quantum mechanics in full detail. A full understanding (and perhaps improvement) of the Born–Oppenheimer picture, for example, will be a hard piece of work (one should, in particular, compare the maximum-entropy decomposition of the thermal non-pure state D_β with that decomposition of D_β which gives the best-localized nuclei in eq. (32); both mentioned decompositions are into nonstationary states).

The nuclear frame of a molecule is definitely an *approximate* classical observable, i.e., superpositions survive (even when the radiation field with all its infinitely many modes is encorporated). Hence an entropy function S_{mean} as for a magnet (describing how fast certain superpositions "die out" with increasing number of spins; see fig. 5) does not exist. Nevertheless similar (though a little bit more complicated) entropy functions can be introduced, describing how fast the distribution p_N of the inversion coordinate q (referring to N modes of the radiation field) con-

verges to the distribution p_∞ with an increasing number N of modes of the radiation field. In large-deviations theory, this sort of entropy is called a *level 2-entropy*, as opposed to a level 1-entropy in fig. 5.

10. Ergodicity breaking and dynamical classical observables

It has been argued in section 9, that two isomeric molecular species are described in usual statistical quantum theory by the same Hamiltonian and hence by the same thermal non-pure state D_β. A similar problem arises with oppositely handed chiral molecules. Hence statistical quantum theory, strictly spoken, cannot explain spectra of isomeric or handed molecules, since thermal *handed* states $D_{\beta,L}$ and $D_{\beta,R}$ or thermal states $D_{\beta,iso}$ for a *particular isomer* are undefined. These thermal states for handed molecules or particular isomers are necessary to discuss spectroscopy via response theory (as discussed in section 3).

One could use the Born–Oppenheimer approximation to define thermal states $D_{\beta,L}$, $D_{\beta,R}$ and $D_{\beta,iso}$: to this end, one must determine the "localized eigenstates" from a chosen minimum of the BO-potential (see section 4) and mix them using the appropriate Boltzmann factors. Here we shall choose a more direct and more comprehensible way of introducing thermal states $D_{\beta,L}$, $D_{\beta,R}$ or $D_{\beta,iso}$, applicable not only to molecules, but to arbitrary systems. It works with *timescales*, and it would actually be interesting to understand the connection of the present approach with time-dependent Born–Oppenheimer approximation.

Note that for the example of a magnet (see fig. 7) consisting of *finitely* many spins the situation is analogous to that one of molecules before: it is no problem to write down the thermal state D_β for the magnet, but it is a problem to define thermal states $D_{\beta,pos.}$ and $D_{\beta,neg.}$ with positive or negative permanent magnetization, respectively.

Using the individual setting of quantum mechanics (as advocated in the present paper), it is no problem to introduce thermal states like $D_{\beta,L}$ and $D_{\beta,R}$. The following "recipe" is ad hoc, but it will become clear later on that this adhoc aspect cannot be avoided. The recipe runs as follows: Take the thermal nonpure state D_β and decompose it according to the *maximum-entropy principle* into an ensemble $\mu_{\beta,max}$ of pure states,

$$\mathrm{Tr}(D_\beta T) = \int_{\substack{\text{all pure} \\ \text{states } \phi}} \phi(T)\mu_{\beta,max}(d\phi) . \tag{94}$$

Suppose now that an approximate classical observable arises, i.e., that the distribution of the expectation values of the inversion coordinate $\hat{q}$ (with respect to the ensemble $\mu_{\beta,max}$) has two sharp peaks (as in the right part of fig. 8). Then $D_{\beta,L}$ and $D_{\beta,R}$ are defined as

$$\text{Tr}(D_{\beta,\text{L}}T) = \frac{\int_{\{\phi|\phi(\hat{q})\leqslant 0\}} \phi(T)\mu_{\beta,\text{max}}(d\phi)}{\int_{\{\phi|\phi(\hat{q})\leqslant 0\}} \mu_{\beta,\text{max}}(d\phi)} \, , \tag{95}$$

$$\text{Tr}(D_{\beta,\text{R}}T) = \frac{\int_{\{\phi|\phi(\hat{q})\geqslant 0\}} \phi(T)\mu_{\beta,\text{max}}(d\phi)}{\int_{\{\phi|\phi(\hat{q})\geqslant 0\}} \mu_{\beta,\text{max}}(d\phi)} \, . \tag{96}$$

The denominator in these equations is introduced to get *normalized* density operators, i.e., density operators D with $\text{Tr}(D) = 1$.

In plain words the recipe can be described as follows: The maximum-entropy ensemble corresponding to the overall thermal non-pure state D_β is divided into two parts, namely into those states having positive expectation value of the inversion coordinate $\hat{q}$ (these are the "right-handed" states in the ensemble) and those having negative expectation value of the inversion coordinate $\hat{q}$ (these are the "left-handed" states in the ensemble). These two respective parts are then integrated up to the density operators $D_{\beta,\text{R}}$ and $D_{\beta,\text{L}}$.

Remark

The spectral decomposition of, say, the density operator $D_{\beta,\text{R}}$ can be expected to give, roughly, the localized eigenstates of the respective Born–Oppenheimer approach. This is the way how the Born–Oppenheimer approach could perhaps be understood. One could also investigate, how the overall thermal non-pure state D_β can be decomposed into pure states in such a way, that the nuclei are localized as much as possible (that is, *not* us the maximum-entropy decomposition). The procedure is always the same: One takes the statistical information, i.e., the overall thermal state, and uses a particular decomposition of this overall thermal state to get information about the pure states. In particular, one would like to know if a molecule has a nuclear frame, or chirality, or isomers, etc. This information about the pure molecular states can then be taken as a starting point for interpretation of single-molecule spectroscopy. In turn, one would like to get information on the pure state of a molecule from single-molecule spectroscopy.

The whole matter is now considered from a *dynamical point of view* (see sections 7 and 8): Under the influence of external perturbations, the pure states of a molecule develop in a stochastic way. The stochastic dynamics on the pure-state space is called *ergodic* if, starting from some initial state ϕ_0, all other pure states can be reached by the stochastic dynamics (for mathematical definitions of ergodicity, see ref. [45]). *For systems with a partial classical structure (chirality, isomerism, magnetization), ergodicity effectively breaks down (with respect to the entire state space):* Starting with a left-handed initial state ϕ_0 of a chiral molecule, for example, the stochastic dynamics will not leave the subensemble of left handed states (for a long time). Hence, the maximum-entropy ensemble corresponding to the "global" ther-

mal density operator D_β will split up into subensembles, which are structurally stable for long times. On the subensembles, the dynamics still acts ergodically. The structurally stable subensembles (for, e.g., left- and right-handed states) behave as attractors, whereas "forbidden" superpositions (of states taken from different structurally stable subensembles) are transient states, finally ending up in one of the structurally stable subensembles.

In this way, density operators like $D_{\beta,L}$, $D_{\beta,R}$ and $D_{\beta,iso}$ can also be introduced by dynamical arguments and the respective approximate classical structure gets a dynamical touch [18]. These density operators correspond to (effectively) stationary distributions of pure states (i.e., to stationary measures on the attractors).

In this dynamical point of view, it becomes again clear that a strict distinction between different isomers or differently handed states is not possible (and not even desirable). There are always some "intermediate", transient states "in between different possibilities" which cannot clearly be assigned to one of them. Think again of left- and right-handed states: one could try to determine the geometry of the transition states during racemization, i.e., the subensemble of states having expectation value of $\hat{q}$ in an interval around $q = 0$. In a way these states do neither belong to the left- nor to the right-handed states.

Recall that one interesting point with chirality is to understand why superpositions of left- and right-handed states are unstable under external perturbations. The idea advocated in this paper is that the maximum-entropy decomposition of the thermal state D_β gives rise to an ensemble μ_{max} which is already concentrated on left- and right-handed states, whereas the probability to find a superposition of left- and right-handed states is very very low (with respect to μ_{max}; in the right part of fig. 8, the value of the density at $q = 0$ is nonzero, but very small). Furthermore, it has been argued in section 7 that the stochastic dynamics of the pure states finally leads (dynamically) to the maximum-entropy ensemble μ_{max}. Hence the idea is that superpositions of left- and right-handed states decay quickly into either a left- or a right-handed state. But this needs further investigation even in the case of mean-field models. In the present section, the problem is no more to show the instability of certain superpositions (this is already settled with the determination of μ_{max}), but to show that the ensemble μ_{max} effectively decays into two (or more) dynamically separated subensembles. Starting with a superposition of states from the subensembles, the stochastic dynamics is expected to lead quickly (in time) into one of those subensembles; and once being in a particular subensemble, the state has almost no chance to get into another subensemble (that is the timescale argument, corresponding to ergodicity breaking). *Hence again:* One expects symmetry reduction (or symmetry breaking) by introducing the maximum-entropy ensemble μ_{max} (of pure states) *and* ergodicity breaking by split of μ_{max} into two or more structurally stable subensembles, in which ergodicity is retained.

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[18] For approximate classical observables with continuous spectrum, the argumentation needs some refinement, since then the approximate classical value changes with time.

Introducing density operators for isomers can be done in the same way, the only difference being that the original "global" ensemble of pure states (corresponding to the overall density operator D_β) is not partitioned into two parts but into as many parts as isomers exist. Again *two* problems come into play: Why are superpositions of isomers unstable *and* why is a particular isomer stable dynamically. Like in the case of chirality one expects symmetry breaking when introducing the maximum-entropy ensemble μ_{max} (of pure states) *and* ergodicity-breaking by split of μ_{max} into two or more structurally stable subensembles. The symmetry breaking corresponds to the instability of superpositions of isomers whereas the ergodicity-breaking corresponds to the structural stability of isomers.

"Isomerism" is, of course, a classical concept, which has been brought into discussion here on a heuristic level. The final goal would be to understand and derive isomerism as an (approximate) classical structure without using any previous chemical wisdom (and starting from an entirely quantum-mechanical description).

Summarizing: Statistical quantum theory imposes too excessive conditions for symmetry breaking and formation of classical structures. In individual quantum mechanics *approximate* symmetry breaking and *approximate* classical structures arise. Strictly spoken, chiral molecules, nuclear frames and molecular isomers do not exist in statistical quantum mechanics. In individual theory, an element of fuzziness comes in which allows introduction of molecular isomerism and the other mentioned concepts.

11. Concluding remarks

Statistical quantum mechanics works surprisingly well, even beyond its scope. Typically, results derived from response theory (see section 3) are applied with good success even for spectroscopy of single molecules.

Nevertheless, some important points in the statistical approach cannot be accepted without discussion:

The thermal density operator D_β must be carefully chosen. Just from the statistical quantum-mechanical formalism alone, it is by no means clear how the thermal state of some isomer or the thermal state of a left- or right-handed molecular species could be defined. As long as the symmetry is not broken "by hand", neither nuclear frame, nor handed molecules, nor molecular isomers appear (see eq. (24) and the discussion concerning uniqueness of the thermal non-pure state in section 9). In the present paper, "symmetry breaking" is derived from the dynamical behaviour, a point of view which was already used in Hund's paper on chirality [68]. The point here is that external perturbations are explicitly discussed (see sections 7 and 8) and that stability under external perturbations necessitates a particular (uniquely determined) decomposition of the thermal non-pure state, namely the maximum-entropy ensemble of pure states corresponding to D_β.

This approach allows to explain that approximate classical structures exist though the superposition principle of quantum mechanics is still fully valid. In particular, the argument that the Stone–von-Neumann theorem [111] excludes classical structures for systems of finitely many degrees of freedom, is relativized: the Stone–von-Neumann theorem indeed excludes *strict* classical observables but it does not exclude *approximate* classical observables. Furthermore, the large-deviation considerations in section 6 show how an approximate classical observable becomes a strict classical observable in the limit of infinitely many degrees of freedom. This limit gives rise to a kind of caricature: The superposition principle is restricted to sectors and does not hold universally any more.

In the present approach, eigenstates of the Hamiltonian do not play a predominant role, but are not excluded either: Only a detailed investigation of maximum-entropy ensembles or the stochastic dynamical behaviour of some molecule (preferably coupled to the radiation field) will finally clarify this question. It might well happen, that the particular context of an empirical situation (level splittings, etc.) determines if eigenstates of the Hamiltonian do indeed arise or not. The sequence of molecular species discussed in Table 1 suggests that "overall eigenstates" (such as the ground state of an ammonia-type molecule) may be unstable and "disappear" when an approximate classical structure (such as handedness) is generated.

Another point should be carefully investigated: In response theory it is assumed that the expectation value of the output observable (see eq. (11)) can be measured without perturbing the state of system. As long as the state of the system differs only slightly from the thermal non-pure state D_β, this is no big problem. But as soon as one starts from a pure state for an individual molecule and tries to apply response theory, things get much more delicate. The fact that entirely different heuristic approaches exist (such as the Bohr–Einstein point of view and the von Neumann point of view) to describe the individual behaviour of molecules (on the pure-state level), should be understood as a warning sign: the individual behaviour of molecules is not clear at all.

Probably, the usual input-output scheme of general system theory should be modified slightly: not only the traditional input $-b(t)B$ used in eq. (5) but also the influence of the measuring device on the state of the system should be considered as input, the output staying the same as usual.

Such a *stochastic quantum-mechanical filtering theory* has not yet been developed. Certainly, it should fit into the response theory described in section 3. There, the thermal non-pure state D_β can be replaced by the maximum-entropy ensemble of pure states, and the individual dynamical behaviour of pure (initial) states is expected to add up to a reasonable dynamics of the corresponding density operator. In such an individual description, the structurally stable subensembles corresponding to molecular isomers or handed species will automatically be worked in. Hence slightly oversimplified dynamics such as given by the Karplus–Schwinger equation (4) will split up into several subdynamics (i.e., dynamics on the subensembles).

Acknowledgements

Appendix 1

STATES OF A TWO-LEVEL SYSTEM

Each pure state of a two-level system is specified by a normalized vector in a two-dimensional Hilbert space

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \quad c_1, c_2 \in \mathbf{C}, \quad |c_1|^2 + |c_2|^2 = 1. \tag{97}$$

Observables, on the other hand, are represented by 2×2-matrices, as, for example, the Pauli matrices

$$\sigma_x \stackrel{\text{def}}{=} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \stackrel{\text{def}}{=} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \stackrel{\text{def}}{=} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{98}$$

Two vectors ξ_1 and ξ_2 describe the same state if the respective expectation values coincide,

$$\langle \xi_1 | T \xi_1 \rangle = \langle \xi_2 | T \xi_2 \rangle. \tag{99}$$

for arbitrary 2×2-matrices T. This is the case if and only if there is some complex number λ such that $\xi_1 = \lambda \xi_2$.

A density-matrix is a positive matrix D with trace 1,

$$\text{Tr}(D) = \text{Tr}\begin{pmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{pmatrix} \stackrel{\text{def}}{=} d_{11} + d_{22} = 1. \tag{100}$$

Sometimes a pure state with state vector ξ is replaced by a corresponding density matrix D_ξ fulfilling

$$\mathrm{Tr}(D_\xi T) = \langle\xi|T\xi\rangle . \tag{101}$$

The density matrix D_ξ gives rise to the same expectation values as the state vector ξ and hence contains the same information. In Dirac bra-ket notation one has

$$D_\xi = |\xi\rangle\langle\xi| . \tag{102}$$

Mixing of pure states ξ_j with appropriate mixing coefficients λ_j results in the expectation values for arbitrary 2×2-matrices T:

$$\sum_{j=1,2,\cdots} \lambda_j\langle\xi_j|T\xi_j\rangle . \tag{103}$$

Here the λ_j are (finitely or infinitely many) positive coefficients fulfilling

$$\sum_{j=1,2,\cdots} \lambda_j = 1 . \tag{104}$$

Mixing of 50% left- and 50% right-handed states, for example, would.need two coefficients $\lambda_1 = \lambda_2 = \frac{1}{2}$. The mixing process (103) gives rise to a non-pure state with density matrix

$$D = \sum_{j=1,2,\cdots} \lambda_j D_{\xi_j} . \tag{105}$$

All density matrices arise in this way as a mixture of pure states. Hence the set of *non-pure states* corresponds precisely to the set of all density matrices. In Dirac bra-ket notation, the density-operator D of the mixing process (103) is given as

$$D \stackrel{\mathrm{def}}{=} \sum_{j=1,2,\cdots} \lambda_j|\xi_j\rangle\langle\xi_j| . \tag{106}$$

Every state which is not pure, i.e., not of the form (102), can be decomposed into pure states. This decomposition can be done in infinitely many different ways. To illustrate this fact, a representation of the state space for a two-level system (including all density operators) will be given. Every density-operator D can be specified by three real numbers, namely the expectation values

$$b_k \stackrel{\mathrm{def}}{=} \mathrm{Tr}(D\sigma_k) \tag{107}$$

of the Pauli matrices, in such a way that

$$D = \tfrac{1}{2}(1 + b_1\sigma_1 + b_2\sigma_2 + b_3\sigma_3) \tag{108}$$

holds. Conversely, an operator of type (108) is a density operator (corresponding to a non-pure state) if and only if the real numbers b_1, b_2, b_3 fulfill

$$|b_1|^2 + |b_2|^2 + |b_3|^2 \leqslant 1 . \tag{109}$$

Hence the state space of a two-level system is (convex) isomorphic to the sphere in real three-dimensional space. The pure states correspond precisely to the points fulfilling

$$|b_1|^2 + |b_2|^2 + |b_3|^2 = 1 , \tag{110}$$

and therefore to points *on the surface S_2* of the sphere. Spin-up and spin-down states correspond to the poles of the sphere. In this representation the mixing process can easily be visualized, since mixing of density matrices corresponds precisely to mixing of the respective 3-vectors defined in eq. (107). The mixing process of eq. (103), for example, corresponds to

$$b_k = \sum_{j=1,2,\cdots} \lambda_j b_{j,k} , \quad k = 1, 2, 3 . \tag{111}$$

Every non-pure state with density operator D (i.e., every interior point of the sphere) is of the form in eq. (106). Nevertheless there exist more general mixtures/decompositions

$$D = \int_{S_2} |\xi_{\vartheta,\phi}\rangle\langle\xi_{\vartheta,\phi}| f(\vartheta, \phi) \frac{\sin \vartheta \, d\vartheta \, d\phi}{4\pi} , \tag{112}$$

where spherical coordinates have been used.

Appendix 2

RULES FOR MARTINGALES

DEFINITION
Consider a probability space (Ω, P) possessing an increasing family of σ-algebras

$$\mathcal{F}_t, t \geqslant 0 . \tag{113}$$

Then a *martingale* is defined as a progressively measurable, *P*-integrable and continuous stochastic process [19] $Z_t = Z_t(\omega)$, $\omega \in \Omega$, $t \geqslant 0$, such that the conditional expectations $E^P[Z_{t_2}|\mathcal{F}_{t_1}]$ fulfill

$$E^P[Z_{t_2}|\mathcal{F}_{t_1}] = Z_{t_1} , \quad 0 \leqslant t_1 < t_2 . \tag{114}$$

For many purposes, it is not necessary to understand this mathematical definition in detail. The important consequences are:

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[19] Again the notation used is not correct. See the corresponding footnote in section 8.

- The integrals over the stochastic variables Z_t's are independent of time [20],

$$\int_\Omega Z_t(\omega)P(d\omega) = \int_\Omega Z_0(\omega)P(d\omega), \quad t \geq 0, \tag{115}$$

- If τ is a stopping time (see section 8), then

$$\int_\Omega Z_{\tau(\omega)}(\omega)P(d\omega) = \int_\Omega Z_0(\omega)P(d\omega). \tag{116}$$

This is a consequence of Doob's optional stopping theorem [127].

Hence martingales are *conserved quantities*, even when they are time-dependent (as functions). It is important to be able to *construct* martingales. This can be done by use of Itô's formula (see below).

Some few rules [44,47] and notations are necessary to deal with a set of d martingales $Z_t := (Z_t^1, Z_t^2, \cdots, Z_t^d)$, e.g., Wiener processes $(W_t^1, W_t^2, \cdots, W_t^d)$ for different coordinate directions $1, 2, \cdots, d$. Note that martingales depend on the "time" t and the stochastic variable ω (the "path"). In the following, all the stochastic integrals are Itô-integrals:

- The joint quadratic variation $[X, Y]$ of two stochastic processes $X_t = X_t(\omega)$ and $Y_t = Y_t(\omega)$ is defined as the stochastic process

$$[X, Y]_t \overset{\text{def}}{=} X_t Y_t - X_0 Y_0 - \int_0^t X_s dY_s - \int_0^t Y_s dX_s. \tag{117}$$

The bracket $[X, Y]$ is called the Doob–Meyer bracket of the stochastic processes X and Y. It is symmetric

$$[X, Y] = [Y, X]. \tag{118}$$

- A stochastic process X is said to be of finite variation if the paths $s \mapsto X_s(\omega)$ are of finite variation for every ω on every finite time interval $[0, t]$. In this case the Doob–Meyer bracket with any other stochastic process Y vanishes, $[X, Y] = 0$.

- For arbitrary stochastic processes, the Doob–Meyer bracket $[X, Y] = [X, Y]_t$ is of bounded variation (and hence not a martingale). The Doob–Meyer bracket for independent Wiener processes $(W_t^1, W_t^2, \cdots, W_t^d)$ can be computed to give

$$[W^i, W^j]_t = t\delta_{ij}, \tag{119}$$

with δ_{ij} being the Kronecker delta.

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[20] Here martingales are always taken with respect to the time t and not with respect to particle number N.

- The Doob–Meyer bracket can be dealt with by observing that

$$\left[\int H_s\,dX_s, \int K_s\,dY_s\right]_t = \int_0^t H_s K_s\,d[X,Y]_s.$$ (120)

- If X and Y are martingales, then

$$X_t Y_t - [X,Y]_t$$ (121)

is again a martingale. The process $(W_t^j)^2 - t$, for example, is a martingale.

- If $F = F(\omega)$ is a real-valued function and if $Z = Z_t$ is a martingale, then the stochastic process

$$\int_0^t F(\omega)\,dZ_s$$ (122)

is a martingale (with respect to t).

- A *semimartingale* Y is defined to be the sum of a martingale Z and a process of finite variation A,

$$Y_t = Z_t + A_t.$$ (123)

Usual functions are of finite variation. The drift part in eq. (60), for example, is of finite variation, whereas the diffusion part is a martingale. Hence the solution of eq. (60) is a semimartingale.

- *Itô's change of variable formula:* Given a differentiable function

$$f : \mathbf{R}^d \to \mathbf{R}$$ (124)

and d continuous semimartingales $X_t^1, X_t^2, \cdots, X_t^d$, then

$$f(X_t) - f(X_0)$$
$$= \sum_{i=1}^d \int_0^t D_i f(X_s)\,dX_s^j + \frac{1}{2}\sum_{i=1}^d \sum_{j=1}^d \int_0^t D_{ij} f(X_s)\,d[X^i, X^j].$$ (125)

Here $D_i f$ is the first partial derivative of the function f with respect to the i-th variable, and $D_{ij} f$ is the second partial derivative of f with respect to the ith and jth variables. Note that Itô's formula is quite general. If, for example, a function h depends on two variables, and if W_t is a Wiener process, then eq. (125) implies that

$$h(W_t, t) - h(W_0, 0)$$

$$= \int_0^t D_1 h(W_s, s) \, dW_s + \int_0^t D_2 h(W_s, s) \, ds + \int_0^t D_{11} h(W_s, s) \, ds, \qquad (126)$$

because $[W_s, s] = 0$ and $[W_s, W_s] = s$ (see above). Since the integral

$$\int_0^t D_1 h(W_s, s) \, dW_s \qquad (127)$$

is a martingale, it follows that $h(W_t, t)$ is a martingale, if

$$D_2 h + D_{11} h = 0 \qquad (128)$$

holds.

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