

*Review***CHIRALITY: A SUPERSELECTION RULE GENERATED  
BY THE MOLECULAR ENVIRONMENT?**

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**Abstract**

The superposition of left- and right-handed forms of a chiral molecule does not exist or is at least very unstable. Frequently, this instability is traced back to the coupling of the molecule to its environment, e.g. the radiation field or collisions with neighbor molecules. The situation is not completely clear, neither theoretically nor experimentally. Here, the theoretical aspects and consequences of the coupling {molecule  $\leftrightarrow$  environment} are discussed.

**1. Introduction**

Physical systems are automatically coupled to their environment and never closed in a strict sense. The influence of the environment may change the system's behavior in a *qualitative* way. A nice example has been proposed by Borel in 1914 ([1], p. 98): There, the influence of a Sirian beetle (of mass 1g,  $8.3 \times 10^{16}$  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 approximately 10 cm after  $10^{-6}$  seconds. The cause seems almost negligible, but nevertheless the effect is enormous.

Here, the coupling between a "small" system (e.g. a molecule) and its environment is studied from a quantum-mechanical point of view. "The" environment, consisting of the rest of the universe, can never be given a precise description. It must therefore be replaced by a model environment which mimics certain aspects of the real situation. One such aspect is the large – eventually infinitely large – number of the environment's degrees of freedom. Environments such as

- the radiation field,
- the gravitation field,
- phonons (if the molecule is embedded into a semi-rigid matrix of other molecules),
- or a "heat bath"

are treated (or may at least be treated) as systems consisting of infinitely many *harmonic oscillators* (see e.g. [2–4]). Hence, the discussion of a molecule coupled

to infinitely many harmonic oscillators can be expected to describe qualitatively the behavior of the joint system {molecule and environment}. A specific model Hamiltonian – the spin–boson Hamiltonian – will be presented in section 3.

From a theoretical point of view, it is indispensable to discuss environmental effects on molecules. The latter are Einstein–Podolsky–Rosen correlated (in short, EPR-correlated) with their environment and therefore cannot be treated as individual objects (cf. [5–9]). Note that EPR correlations lead to measurable effects [10] even if these systems are entirely separated and without any interacting force! It is not sufficient to replace the environment by an additional potential: A complete discussion of the joint system {molecule and environment} is necessary. Nevertheless, there is a chance that an essential part of this joint system behaves again like an object, i.e. is not EPR-correlated with the rest of the system. Such an essential part will be called a *quasimolecule*. Under suitable conditions it behaves just as the isolated molecule apart from some restrictions. These restrictions may, for example, refer to the states of the quasimolecule, "forbidding" certain superpositions (see section 2) of state vectors.

*The isolated quantum-mechanical molecule is a purely theoretical construction, whereas the quasimolecule is the reference point of the experimentalists.* One may compare this with the situation of an ion brought into solution. The solvated ion carries some layers of water molecules, which changes its mass and its mobility in an electric field. The solvated ion *corresponds* to the above quasimolecule. The already mentioned spin–boson Hamiltonian permits us to *derive* (see section 4) a quasimolecule with a superselection rule (see section 2).

Sometimes it is useful or even necessary to replace a quantum environment by a classical one, i.e. a (classical) stochastic process such as Brownian motion or white noise [11–13]. This paves the way to environments built up of "*collisions with neighbor molecules*" (cf. [14–20]) or to "*Onsager-type reaction fields*" (cf. [12,16]).

## 2. Superselection rules

Handedness of molecules is an interesting property: A (single) molecule is *either* left- or right-handed and any compromise seems to be excluded. This fact contradicts a basic postulate of traditional quantum mechanics [21], the "superposition principle". It says that the superposition

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

of two state vectors  $\Psi_1$  and  $\Psi_2$  with complex coefficients  $c_1, c_2$  (properly normalized) is again a legitimate state vector of the system in question.

Superposition of left- and right-handed state vectors gives rise to a kind of intermediate form. A symmetric choice of the constants  $c_1 = c_2$  (or  $c_1 = -c_2$ ) would result in a space-inversion invariant state and thus a molecular species which does *not* rotate the plane of polarization of light. If the left- and right-handed forms have

a well-defined nuclear frame, the same is no longer true for their superpositions. The traditional chemist's conception of a molecule is not compatible with the superposition principle.

The expectation value of an arbitrary observable  $T$  with respect to the state vector  $\Psi$  of eq. (1) is given by

$$\begin{aligned} \langle \Psi | T \Psi \rangle &= |c_1|^2 \langle \Psi_1 | T \Psi_1 \rangle + |c_2|^2 \langle \Psi_2 | T \Psi_2 \rangle \\ &+ (c_1)^* c_2 \langle \Psi_1 | T \Psi_2 \rangle + c_1 (c_2)^* \langle \Psi_2 | T \Psi_1 \rangle. \end{aligned} \quad (2)$$

Here,  $\langle \cdot | \cdot \rangle$  is the ordinary scalar product for state vectors in the underlying Hilbert space (cf. e.g. [22]). As observables  $T$  one may, for example, consider position and momentum operators or spin operators. If the "transition probabilities"  $|\langle \Psi_1 | T \Psi_2 \rangle|^2$  and  $|\langle \Psi_2 | T \Psi_1 \rangle|^2$  vanish for *arbitrary* observables  $T$ , one says that the state vectors  $\Psi_1$  and  $\Psi_2$  are *separated by a superselection rule* (cf. [23]). The expectation value (2) is then given for arbitrary  $T$  as

$$\langle \Psi | T \Psi \rangle = |c_1|^2 \langle \Psi_1 | T \Psi_1 \rangle + |c_2|^2 \langle \Psi_2 | T \Psi_2 \rangle, \quad (3)$$

i.e. as a weighted sum of expectation values  $\langle \Psi_1 | T \Psi_1 \rangle$  and  $\langle \Psi_2 | T \Psi_2 \rangle$ . If such a decomposition exists, one calls the expectation value (3) a *mixed state*; otherwise, it is called *pure*. Mixtures correspond to a statistical ensemble (e.g. a racemate), whereas an individual system (e.g. a single molecule) is described by a pure state (cf. [24,25]). *Note that here only single molecules are under discussion and never racemates!*

If the superposition (1) leads to a pure (respectively, mixed) state, it is called *coherent* (respectively, *incoherent*). Incoherent superpositions of pure states, i.e. superpositions leading to a mixed state, leave the domain consisting of pure states. This fact is ordinarily expressed by saying that "*incoherent superpositions are forbidden*". This diction refers to the distinct interpretation of mixed and pure states, but does *not* forbid mixed states as such.

The above definition of a superselection rule is a little sloppy since various different state vectors may give rise to the same expectation value, that is, to the same state. Hence, for two states to be separated by a superselection rule one has to require that the transition probabilities between arbitrary state vectors implementing them vanish.

In traditional Hilbert-space quantum mechanics, superselection rules do not appear in a natural way. Sometimes they can be introduced ad hoc, excluding certain state vectors without a proper foundation. Here, the question will be posed if superselection rules can be *derived without ad hoc assumptions*.

Superselection rules arise with most commonplace phenomena: The motion of a billiard ball, for example, can be described perfectly in quantum mechanics by wave packets. Superposition of two wave packets, centered around different positions, leads to a state which has no (even vaguely defined) position anymore. Multiple superposition of wave packets might be used to prepare a billiard ball in a box as a standing wave (cf. [26,27]). This contradicts commonplace experience.

For chiral state vectors, a superselection rule seems to appear if the difference between the energy of the (symmetric, space-inversion invariant) ground state and the energy of the first excited state (with reference to vibrations of the nuclei) is very small. For the amino acid alanine, this energy difference has been estimated in [28] as lying around  $10^{-70}$  atomic units. Alanine seems to be chiral (in the sense of a superselection rule). The corresponding energy difference for ammonia (or its potentially chiral derivate NHDT) is around  $10^{-7}$  atomic units. For ammonia, it seems possible to prepare arbitrary superpositions [29], for example, the proper ground state (without nuclear frame!) or the "pseudochiral" pyramidal states. The former is stationary, whereas the latter tunnel back and forth. Handed states are called "pseudochiral" if they are *not* separated by a superselection rule.

*The problem of chirality cannot be settled by the generally accepted argument of Hund [30], which says that chiral states – once prepared – are stable for a very long time. This argument does not answer the questions: "Why have superpositions of chiral states not yet been prepared?" or "Are superpositions of chiral states particularly unstable?" (cf. [31]). Note that the case of billiard balls is a completely analogous one.* There, the argument of Hund corresponds precisely to the argument of Born [27] saying that wave packets – once prepared – are stable for a very long time. Again, questions concerning superpositions remain unanswered, a fact which was stressed by Einstein [26,27].

Certain superpositions are perhaps short-lived and not easily detectable. For the specific situation of chirality, an experiment preparing superpositions of chiral states has been proposed by Quack [32,19]. This experiment refers to an *isolated chiral molecule in the Born–Oppenheimer approximation*. The electronic ground-state potential is supposed to be of double-minimum form. The potential for the electronically excited state is supposed to have only one minimum. "Chiral" states of the molecules can then but exist for the electronic ground state and not for the excited one. According to the usual selection rules, one should have a non-zero transition probability between the (spectroscopically prepared) non-chiral excited state and the superposition of the chiral ground states. The superposition of chiral ground states should thus be accessible by spectroscopic methods. It could be detected and distinguished from chiral states, since the respective selection rules are different.

Perhaps it is not so relevant if superpositions are short-lived (see section 6) or do not exist at all. *Both variants are more closely related than might appear at first sight.* First, the latter variant is discussed (sections 3 and 4). It is shown that *superselection rules can be derived by considering the coupling of a molecule to an environment with infinitely many degrees of freedom.*

### 3. The spin–boson Hamiltonian as a model for the coupling of a molecule to its environment

The spin–boson Hamiltonian discussed here describes the coupling of *one* spin (= a two-level system) to an environment consisting of *infinitely many* harmonic oscillators (bosons):

$$H = \hbar \varepsilon \sigma_1 \otimes I \quad (4a)$$

$$+ I \otimes \sum_{n=1}^{\infty} \hbar \omega(n) a_n^* a_n \quad (4b)$$

$$+ \hbar \sigma_3 \otimes \sum_{n=1}^{\infty} \lambda(n) \{ a_n + a_n^* \}. \quad (4c)$$

Part (4a) corresponds to the isolated spin, part (4b) to the free environment, and part (4c) to the coupling between spin and environment.

The observables of the two-level system are  $2 \times 2$  matrices, in particular the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (5)$$

The two-dimensional Hilbert space of the spin can be thought of as being built up of a ground state and an excited state of the molecule. As parameters of this molecular caricature, only the level splitting  $\varepsilon$  enters. The Hamiltonian of the isolated spin (= the isolated molecule) is given by (4a), with  $2\hbar\varepsilon$  being the difference of the corresponding energy eigenvalues.

The observables of the environment are "boson operators"  $a_n$ ,  $n = 1, 2, \dots$ , and their adjoints  $a_n^*$  fulfilling the commutation relations

$$[a_n, a_{n'}] = 0, \quad [a_n, a_{n'}^*] = \delta_{nn'}. \quad (6)$$

Here,  $\delta_{nn'}$  is the Kronecker delta (0 or 1, depending on whether  $n$  and  $n'$  are different or identical). The boson operators can be replaced by position and momentum operators, related by

$$a_n =: (2\hbar)^{-1/2} \{ (m(n)\omega(n))^{1/2} Q_n + i(m(n)\omega(n))^{-1/2} P_n \}, \quad n = 1, 2, \dots \quad (7)$$

The masses  $m(n) > 0$  can be fixed arbitrarily. The frequencies  $\omega(n)$  – already arising in (4b) – are supposed to be strictly positive.

The Hamiltonian of the isolated environment (4b) consists of Hamiltonians for harmonic oscillators with frequencies  $\omega(n)$ . Writing these Hamiltonians in the form

$$\hbar \omega a^* a \quad (8)$$

is already very helpful when only a single harmonic oscillator is discussed (see [22], section 12.6). The boson operator  $a^*$  is often called a "creation" operator, whereas  $a$  is sometimes called an "annihilation" operator, since they allow us to go up and down the eigenvalues of (8). The zero-point energy is omitted here. It gives but a shift of the energy scale and diverges for infinitely many modes. In a precise discussion, one would replace the Hamiltonian (4) by the respective Heisenberg dynamics (cf. [33]). Anyway: Omitting the zero-point energy is perfectly legitimate and not just a trick to obtain something reasonable. Every harmonic oscillator is coupled to the spin by a dipole-type coupling (4c) with a real coupling constant  $\lambda(n)$ . Instead of countably many modes, one could use continuously many. Here, only the most simple version is considered. Physically, this does not change very much.

The frequencies and coupling constants should fulfill the condition

$$\sum_{n=1}^N \frac{|\lambda(n)|^2}{|\omega(n)|} < \infty. \quad (9)$$

This guarantees that the Hamiltonian (4) is bounded below, i.e. the respective energies cannot be arbitrarily negative.

The spin–boson Hamiltonian is invariant under the space-inversion symmetry  $\iota$

$$\iota(\sigma_1) := \sigma_1, \quad (10a)$$

$$\iota(\sigma_2) := -\sigma_2, \quad (10b)$$

$$\iota(\sigma_3) := -\sigma_3, \quad (10c)$$

$$\iota(a_n) := -a_n, \quad n = 1, 2, \dots \quad (10d)$$

Left- and right-handed states are transformed into one another by this symmetry.

*The spin–boson Hamiltonian is one of the few model Hamiltonians for the coupling of a "small system" (e.g. a molecule) to its environment.* It can be derived from the coupling of a molecule to the radiation field (cf. [28,34–37]) by using certain approximations (see section 5). The spin–boson Hamiltonian arises in other contexts, as for SQUIDS or the coupling of a "small system" to phonons (cf. [3,38,20]). Here, the spin–boson Hamiltonian is particularly interesting since one can – depending on the parameters  $\varepsilon$ ,  $\omega(n)$ ,  $\lambda(n)$  – derive a superselection rule.

#### 4. Derivation of superselection rules for the spin–boson model

The Hamiltonian (4) may be written down for *finitely* many modes of the environment and is then uniquely defined up to multiplicity. This is a consequence of the *theorem of Stone and Von Neumann* ([22], section 12.3). It says that the Heisenberg commutation rules<sup>1)</sup> [39] (or the Boson commutation rules (6)) determine the respective position and momentum operators (boson operators) uniquely up to multiplicity. It is then legitimate to use the Schrödinger representation of position and momentum operators  $\{Q_{\text{SCHR}}, P_{\text{SCHR}}\}$  on the Schrödinger Hilbert space denoted here by  $\mathcal{H}_{\text{SCHR}}$ . "Up to multiplicity" means that the Schrödinger representation can be blown up by tensoring an additional Hilbert space  $\mathcal{H}$  leading to position and momentum operators

$$Q := Q_{\text{SCHR}} \otimes I, \quad (11a)$$

$$P := P_{\text{SCHR}} \otimes I \quad (11b)$$

on the Hilbert space

$$\mathcal{H}_{\text{SCHR}} \otimes \mathcal{H} \quad (12)$$

instead of the original ones. The unit operator  $I$  acts trivially on  $\mathcal{H}$ . Multiplicity does not change the interrelations between the operators built up from position and momentum operators, and hence does not change the physics based on these position and momentum operators (cf. [33], definition 4). It follows that all representations of the Heisenberg or boson commutation relations are physically equivalent for *finitely* many degrees of freedom (= finitely many position and momentum operators).

For *infinitely* many degrees of freedom, this result breaks down. There exist (myriads of) *physically inequivalent representations* of the commutation relations (6) on Hilbert spaces. "Representation" means that operators  $a_n$  and  $a_n^*$ ,  $n = 0, 1, 2, \dots$ , exist – acting on some Hilbert space – which fulfill the commutation relations (6). A particular example is the *Fock representation* (see [22], section 15.5) on the *Fock–Hilbert space*  $\mathcal{H}_{\text{F}}$ . The Hilbert space for the full spin–boson model (and not just the boson field) in the Fock setting is given as a tensor product with a two-dimensional Hilbert space  $\mathbb{C}^2$

$$\mathbb{C}^2 \otimes \mathcal{H}_{\text{F}}. \quad (13)$$

The  $2 \times 2$  matrices act naturally on this Hilbert space, namely, as before on  $\mathbb{C}^2$  and trivially on  $\mathcal{H}_{\text{F}}$ . The  $2 \times 2$  matrices referring to the spin can always be introduced in a similar way and do not present any additional difficulties.

<sup>1)</sup>To exclude pathological cases, the Heisenberg commutation rules must be replaced by their exponential form (see [39], section VIII.5).

Historically, the Fock representation played an important role. It is characterized by the condition that the Hamiltonian (4b) of the free boson field admits a ground state, the so-called Fock state or vacuum. Exclusive use of the Fock representation would perpetuate the situation of the Stone–Von Neumann scheme. However, note that the Fock representation does *not* admit superselection rules! Hence, the *exclusive* use of the Fock representation leads to empirically incorrect results. On the formal level, already scaling transformations (scaling the position and momentum operators in a way to preserve the Heisenberg commutation relations) lead out of Fock space! Hence, one should *not exclusively* restrict attention to the Fock representation.

"Physical inequivalence" can be given a precise definition (cf. [33], definition 5). Here, only some aspects of physical inequivalence are considered:

- There exist representations admitting superselection rules and some which do not. Representations of the former and latter type are definitely not physically equivalent.
- The spin–boson Hamiltonian is well defined in some representations but not in all of them. As already stated, there is no difficulty in defining the spin–boson Hamiltonian for finitely many modes of the field and "well defined" is to say that the infinite-mode limit of these Hamiltonians exists.<sup>2)</sup>
- If Hamiltonians exist in two representations, both corresponding to the formal spin–boson Hamiltonian (4), their spectral structure can still be very different. For example, one of them may admit a ground state and the other not. A "ground state" is characterized just as in ordinary quantum mechanics as an eigenstate of the Hamiltonian with an eigenvalue at the lower end of the Hamiltonian's spectrum.

The use of representations physically inequivalent to the Fock representation can be nicely illustrated by the spin–boson model. The spin–boson Hamiltonian can be properly defined in the Fock situation, i.e. on the Hilbert space (13). Depending on its parameters (level splitting, frequencies, coupling constants), it may admit a ground state or not. In the former case, this ground state is the only one in Fock space. In the latter case, it still has (at least two) ground states, but these ground states do not live in Fock space (more precisely: in the Hilbert space (13)) but in other representations.

For the spin–boson model with non-zero level splitting  $\varepsilon \neq 0$  (and a broad class of representations, see [40]), the following holds: Let  $\Psi_1$  and  $\Psi_2$  be different ground states of the spin–boson Hamiltonian (in some fixed representation). *Then  $\Psi_1$  and  $\Psi_2$  are separated by a superselection rule. In particular, there is a superselection rule separating ground states which are mirror-images of each other, i.e. related to each other by the transformation (10).* Hence, all transition probabilities  $|\langle \Psi_1 | T \Psi_2 \rangle|^2$  vanish, where  $T$  is some arbitrary operator built up from boson operators and spin

<sup>2)</sup> This limit is taken in the strong resolvent sense (see [39], section VIII).



matrices. "Built up" means that one may use polynomials of the mentioned operators (e.g.  $27a_{234}a_3^* + \sigma_1 a_{55}$ ) and limits [33] of such polynomials.

Hence, if one can show that there exist ground states with a mirror-image relationship, then these ground states are separated by a superselection rule. In other words: These ground states are chiral. If there is no superselection rule, then only one ground state exists which, incidentally, lives in a Fock situation with Hilbert space (13) [41]. This latter case corresponds to the situation of ammonia in the heuristic discussion above.

Ground states of the spin-boson model with a mirror-image relationship can only appear if the coupling constants  $\lambda(n)$  behave suitably for low frequencies: The condition

$$\sum_{n=1}^N \frac{|\lambda(n)|^2}{\omega(n)^2} = \infty \quad (14)$$

for the so-called "*infrared singularity*" (in short: IR-singularity) has to be fulfilled [28,41]. The "strength" of the IR-singularity is measured by the coefficient  $\zeta$  in the proportionality relation

$$\sum_{n=1}^N |\lambda(n)|^2 \exp \{-\omega(n) |t|\} \propto |t|^{-\zeta} \quad (\text{for large times } |t|). \quad (15)$$

For  $\zeta$  strictly larger than 2, there is no IR-singularity. This situation is called "superohmic" in the terminology of Leggett [3]. The physically most important case with  $\zeta = 2$  is called "ohmic": condition (14) is fulfilled. For  $1 < \zeta < 2$ , condition (14) is again fulfilled and the IR-singularity is called "subohmic". In the superohmic situation, one has no superselection rule *with respect to ground states*. For ohmic and subohmic behavior, one may get ground states separated by a superselection rule (depending on the parameters  $\varepsilon, \dots$ ). The *coupling strength*  $\rho$  in figs. 1 and 2 is the proportionality constant of relation (15).

For an ohmic/subohmic IR-singularity, the "phase diagrams" of figs. 1 and 2 proposed by Spohn arise ([40–44], summarized in [33]).

In the ohmic case, it is necessary to have a certain coupling strength to get ground states which are separated by a superselection rule. In the subohmic situation, one gets a superselection rule for every coupling strength if the level splitting  $\varepsilon$  is small enough (but not necessarily zero). For the special case  $\varepsilon = 0$ , a superselection rule arises for arbitrary coupling strength, if the IR-singularity holds. This is not revealed in the figures.

*The spin-boson Hamiltonian gives rise to superselection rules for a suitable choice of its parameters. The derivation of these superselection rules is based on a purely quantum-mechanical starting point. Note that the spin-boson Hamiltonian is a model: Hamiltonians of realistic situations can only be brought to the form of the spin-boson Hamiltonian by (severe) approximations.*

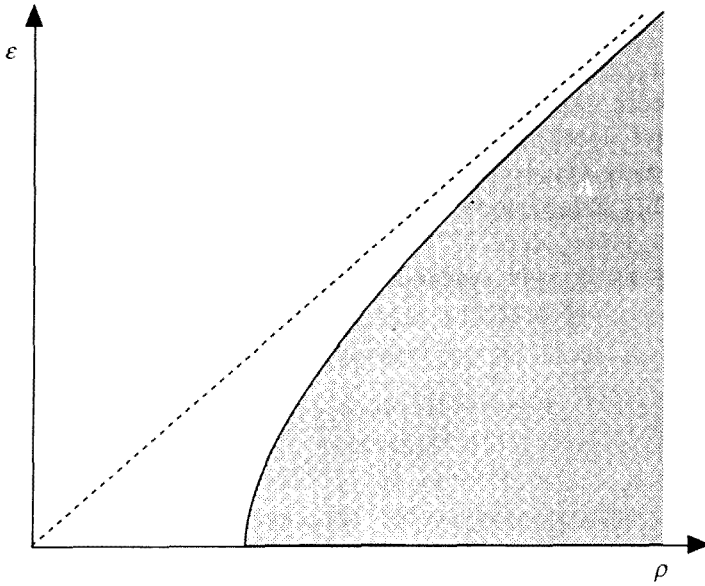


Fig. 1. Phase diagram of the spin-boson model with *ohmic* IR-singularity depending on the level splitting  $\epsilon$  and the coupling strength  $\rho$ . A superselection rule arises for parameters in the shaded region.

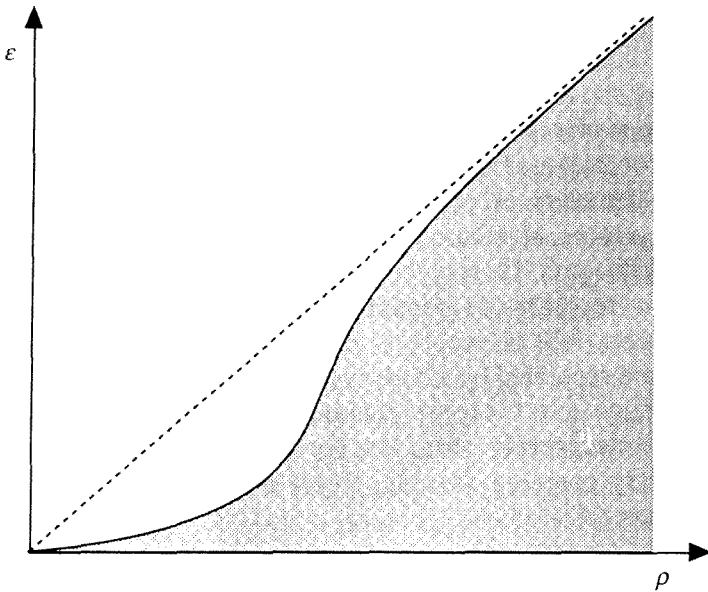


Fig. 2. Phase diagram of the spin-boson model with *subohmic* IR-singularity depending on the level splitting  $\epsilon$  and the coupling strength  $\rho$ . A superselection rule arises for parameters in the shaded region.

## 5. Does the radiation field generate molecular superselection rules?

The Hamiltonian for the joint system {molecule and radiation field} (cf. [34,36,37]) can be brought into the form of the spin–boson Hamiltonian by certain approximations: The molecule has to be replaced by two suitable states (e.g. the ground state and some excited state). Furthermore, one has to

- (i) omit the so-called  $A^2$ -term (where  $A$  is the vector potential of the radiation field), *or*
- (ii) introduce the dipole-approximation [37].

*Both approximations (i) and (ii) are severe interventions.* In case (i) one gets an ohmic IR-singularity [28], whereas for (ii) the IR-singularity is eliminated altogether (cf. [37], section A<sub>IV</sub>.2, and [45,46]).

The generation of chiral ground states by the radiation field was proposed for the first time by Pfeifer in this thesis [28]. He used a variational principle for Hartree (= product) states. His phase diagram does not differ for the ohmic and subohmic situation. The borderline between the two relevant regimes (with or without superselection rule) is given by the dotted line in figs. 1 and 2. Asymptotically (for large coupling strength), the phase diagram by Pfeifer coincides with the correct ones of figs. 1 and 2. For certain spin–boson Hamiltonians with more than two "molecular" levels it seems that the correct diagrams approach more and more the diagram proposed by Pfeifer [47].

The discussion of ground states of the full Hamiltonian for the joint system {molecule and environment} is difficult and unsettled up to now. Hence, the question in the title of this section remains open. One should perhaps *go beyond ground states*. It can be made plausible [48] that *pure* states should be used, *but these pure states need not necessarily be ground states or even stationary states*. Superselection rules arise in all systems with infinitely many degrees of freedom, even for the radiation field without an IR-singularity.

## 6. Is molecular chirality generated by collisions with neighbor molecules?

"Collisions" with neighbor molecules could be responsible for the destabilization of superpositions of chiral states (cf. [14,19,20]). Usually, the dynamics for such a process consists of two parts, one for the isolated molecule and another special one for the collisions. It is then a standard assumption that a collision of the considered chiral molecule produces a "*dephasing*", i.e. the molecule is *localized* in one of the wells of its double-well potential. In the present context, "localized" is to say that the molecule acquires an approximate nuclear frame, corresponding to the position of the respective well.

The dynamics used is a linear density operator dynamics, eventually a semigroup, e.g. of Bloch type. Taking the localized states, say  $\Psi_L$  and  $\Psi_R$ , as basis

vectors, the "dephasing" is described by the shrinking of the outer-diagonal elements of the respective density matrix.

The dephasing assumption is perhaps supported by experimental results (cf. [49–51,29]). The first three cited papers refer to the pressure dependence of the ammonia inversion spectrum, the last one to molecular beam experiments. Ammonia under high pressure shows a "collision" broadening of the inversion line and the approximate resonant frequency tends to zero at a pressure of about 2 atmospheres. One interpretation of these facts might be that the totally symmetric form of ammonia is destabilized by collisions. This interpretation is not actually confirmed, neither theoretically nor experimentally. On the theoretical side, it should be mentioned that a molecule's localization is a *measurement-type process* which is notoriously difficult to derive.

An example for the *derivation* of measurement-type processes has been given in [12,52]. There, the starting point is a spin–boson Hamiltonian of type (4). As a result, one obtains a Schrödinger–Langevin stochastic differential equation which eventually could accomplish the prescribed goal.

Collisions with neighbor molecules can be described by perturbation of the molecular parameters. Think of a (Born–Oppenheimer) double-minimum potential which is stochastically perturbed. This gives again rise to a stochastic differential equation, sending *pure* states of the molecule into *pure* states. "Stochastic" means that the state of the environment is not fixed uniquely (but only with a certain probability). The dynamics of the molecular state depends of course on the state of the environment. Hence, all statements, e.g. on localization, are probabilistic. Averaging over all possible states of the environment then results in a density operator dynamics (see above). The dynamics for pure states corresponds to an ontic interpretation, describing a *single* molecule. The associated density operator dynamics refers to an epistemic interpretation, describing a statistical ensemble. More precise information is given by the dynamics for pure states. The density-type dynamics might even be compatible with different dynamics for pure states (or with no one at all) and hence is difficult to interpret.

Depending on the molecular and environmental parameters, one might expect a (dynamical) localization with respect to the BO-potential. Such a process would correspond to the first variant of a superselection rule mentioned at the end of section 2: "Superpositions are short-lived and decay into their constituents". Results in this direction do not seem to exist. Nevertheless, the results of [53–56] could be considered as a hint in the direction mentioned. In these papers, it is shown that a "small" stationary perturbation of the double-minimum potential leads to localized eigenfunctions. These results cannot be directly applied to the problem of chirality *as defined above* (see section 2), since they in no way forbid the *superposition* of localized (eigen-)states. A similar remark could be made concerning solutions of the chirality problem based on *weak interactions/parity violation/weak neutral current* (cf. [57,32,58]). If the Hamiltonian loses its space-inversion symmetry by weak

interaction terms, then the eigenfunctions have a tendency to be "localized", but superposition is *not* forbidden!

In [16], a mechanism for the stabilization of localized states is presented: Localization leads to a nonvanishing dipole moment  $\langle \hat{\mu} \rangle$ . This dipole moment polarizes the environment and generates a reaction field  $\mathcal{E}_R$ , collinear with  $\hat{\mu}$  so that the interaction  $-\hat{\mu} \mathcal{E}_R$  is negative and tends to stabilize the nonsymmetric state under consideration. The above-mentioned Schrödinger–Langevin equation [12,52] could serve as a model for this process since it exhibits various types of reaction fields.

## 7. Concluding remarks

The problem of chirality is a special version of the more general question asking for the origin of superselection rules. The deeper reason for these problems is the *incompatibility between the formalism of traditional quantum mechanics* [21] *and the commonplace experience that superselection rules exist*. It is a modest modification (with dramatic physical consequences) not to insist any longer on the Fock representation of the boson commutation rules (6). Considering arbitrary representation of (6) opens the way for a proper discussion of infinite systems: Superselection rules arise and the "only" problem is to choose physically sensible ones. "Small" systems (e.g. molecules) may acquire superselection rules through the coupling to an environment with infinitely many degrees of freedom (see section 4). The problem of chirality can then be discussed as a problem of stability: Superpositions of chiral states seem to be unstable under outer perturbations. Unfortunately, this conception has yet the status of a conjecture. For none of the discussed environments have superselection rules been derived rigorously. Precise results can be obtained only for the semirealistic spin–boson Hamiltonian (and related models).

The experimental situation is not very satisfactory either. All presently available experimental evidence is compatible with the idea that chirality – and all other above-mentioned candidates – are indeed superselection rules. Nevertheless, it could be that nobody has tried with enough skill to prepare superpositions of chiral states. Eventually, these unstable states could be prepared by the screening of all outer influences (radiation field, collisions, . . .).

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