

## THE POLYMER CONFORMATIONAL STABILITY AND TRANSITIONS: A QUANTUM DECOHERENCE THEORY APPROACH

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### ABSTRACT

In this paper we describe the problem of polymer conformational stability and transitions in the framework of the so-called quantum decoherence theory. We propose a rather qualitative scenario yet bearing generality in the context of the quantum decoherence theory, enabling us to reproduce both, existence and stability of the polymers conformations, *and* the short time scales for the quantum-mechanical processes resulting effectively in the conformational transitions. The proposed model is qualitative yet providing us with the possibility to *overcome the main obstacle* in resolving the problem of (semi-)classically unreasonably long time necessary for the change of conformation of the polymers in a solution.

### 1. INTRODUCTION

The long standing problem of the polymer conformational transitions is an open issue of the cross-disciplinary research work and interest [1-4]. It is usually referred to as the Levinthal's paradox with an emphasis on the substantial discrepancy between the phenomenological data and the theoretical background of the issue [5]. The original Levinthal's analysis [5] has led to extensive search for the so-called „preferred pathways (trajectories)“ in the conformation space of a macromolecule. Recently, the problem is sharpened by the new approach that calls for the funnel-like form of the conformation space [6], probably offering the possibility to overcome the Levinthal's paradox.

In this paper, we offer *a new approach* to the problem. Actually, we show that the fully *quantum-mechanical* approach within the so-called decoherence theory [7] offers both, existence and stability of the molecules conformations, *and* the rather fast decoherence-like transition between the different conformations. Within our approach, the Levinthal's paradox completely disappears.

### 2. THE PROBLEM

In this section, we precisely outline the problem we are interested in.

#### 2.1 The Born-Openheimer approximation

It is well-known that the Born-Oppenheimer adiabatic approximation establishes geometrical shape of a molecule. The atoms (atomic groups) constituting a molecule are imagined to be placed in the vertices of certain three-dimensional (3D) shape as illustrated in Fig. 2.1.

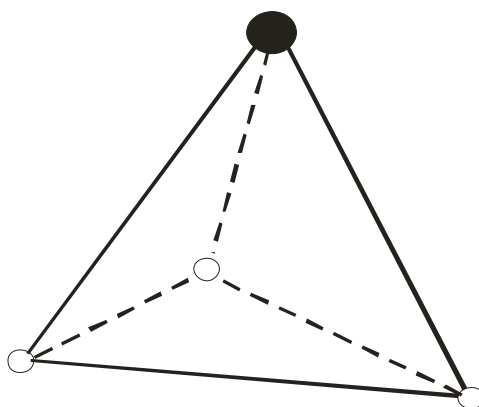


Fig. 2.1 The ammonia molecule geometric (pyramidal) shape/form

At the zeroth approximation, the atoms (more precisely: atomic groups) sitting in the vertices are frozen - their oscillations around the equilibrium positions being neglected. In reality, the atoms are rather quickly vibrating thus giving rise to the fast changes of the molecule's shape, which, on average, is presented by the zeroth approximation shape. Yet, a word of caution is worth saying in this regard.

The geometrical forms of the molecules should not be too literally understood/interpreted. Even in the zeroth approximation, the molecule's shape is subject to the Heisenberg (position vs. momentum) uncertainty relation. However, the *relative positions* of the atoms are still well-defined variables. These variables' quantum-mechanical *averages* justify the zeroth approximation as defined above. Fortunately enough, these relative positions can be „measured“ by the low energy particles. Bearing these subtleties in mind, one may consider the molecules *effectively* to bear the „definite“ geometrical shapes - as it is *generally assumed* in chemistry.

## 2.2 The molecules conformations

The larger molecules are always found in oriented states, which assume the definite geometrical form in the sense of the preceding section. In the simplified terms, the larger molecules may be viewed as the 3D (semi-)classical clusters as presented in Fig. 2.2.

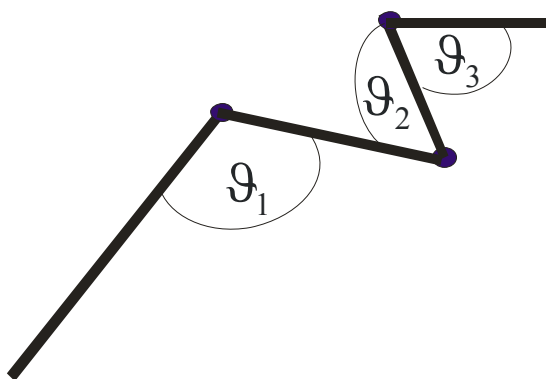


Fig. 2.2 A 3D cluster (semi-)classically representing a molecule. The vertices are occupied by the atoms/atomic-groups, the straight lines representing the chemical valence-bonds.

Actually, the explanation of the molecules' optical activity originates from the assumption that the different geometrical forms of the molecules, being energetically different, necessarily give rise to different responses upon the external optical stimulus. More precisely: The relative distances as well as the valence-angles (cf. Fig. 2.2) between the adjacent atoms (atomic groups) are *well-defined* variables of the molecules so much as they can be referred as to the *molecules' conformations*. Furthermore, the different conformations of a molecule are mutually related by *conformational transitions* - the geometrical transformations keeping the mutual distances of the

atomic groups as well as the valence-angles ( $\vartheta_i$ ) as depicted above – allowing (semi-)classically for a succession of local rotations of adjacent molecular segments over the preceding valence-bonds. While keeping the primary structure of the molecules, the conformational transformations effect in the different (bio)chemical 3D-structurally-dependent activity of the molecule subjected to the transformation.

The experimental evidence [1-4] in this regard can be described (summarized) as follows: The molecules *dissolved in a liquid* are found both to bear as well as to maintain their geometrical shapes/forms - which refers to every single molecule in the liquid. Therefore, in a liquid, the molecules' forms can be described by a *statistical ensemble of shapes (conformations)* generally depending on the parameters of the composite system „molecules + liquid“ - such as the composition, temperature, viscosity etc. For the fixed parameters of the system, the above-mentioned ensemble maintains its definition - which we here refer to as the *stationary state*: in general, the concentration of the molecules bearing a given shape (from the set of the possible conformations) is constant. In other words: If left intact, the ensemble will maintain its state. However, certain external actions can give rise to the change of the conformations of the molecules in the liquid [8]. Such external action can be described as the *nonstationary process*, which finally gives rise to the relaxation process eventually leading to the *new stationary state* of the system, with different concentrations of the conformations, including (possibly) appearance of the new ones.

Therefore, in simplified terms, the evidence about the conformations can be described as follows:

- (i) A stationary state is initially defined by the molecules' conformations (statistical) distribution/concentration, which remains intact as long as the stationary state is conserved,
- (ii) Certain external actions can destroy the stationary state, and can be characterized by the change of the composite system's parameters,
- (iii) The external action eventually gives rise to the relaxation process, which, in turn,
- (iv) Gives rise to another stationary state, which is characterized by another conformation distribution/concentration.

### 2.3 Levinthal's paradox: A survey

Due to the influence of the environment, the large molecules may *change their conformations*. According to Fig. 2.2, these changes can be viewed/interpreted as the externally induced deformations of the 3D molecular cluster as presented in Fig. 2.3. For instance, the *successive, local* rotations can effect in change of the lattice shape. These conformational transformations keep both, the relative positions of the vertices as well as the angles characterizing the initial conformation.

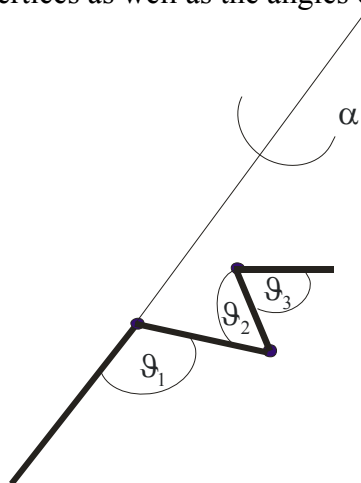


Fig. 2.3 Conformational transition by the (semi-)classical local rotation for the angle  $\alpha$  in the 3D molecular cluster. Here, only the segment defined by the valence-angles  $\vartheta_{2,3}$  rotates over the preceding chemical valence-bond, coinciding with the axis of rotation.

Physically, the different conformations of a molecule are described by the different (conformational) energies ( $V(k)$ -minima in Fig. 2.4) of the molecule [1-4]. Actually, even for the „frozen“ molecule (neglected vibrational degrees of freedom), the different conformations are ascribed the different energies. Denoting the conformation,  $K$ , as the molecules variable, the molecular electronic energy dependence on  $K$  can be qualitatively presented by Fig. 2.4.

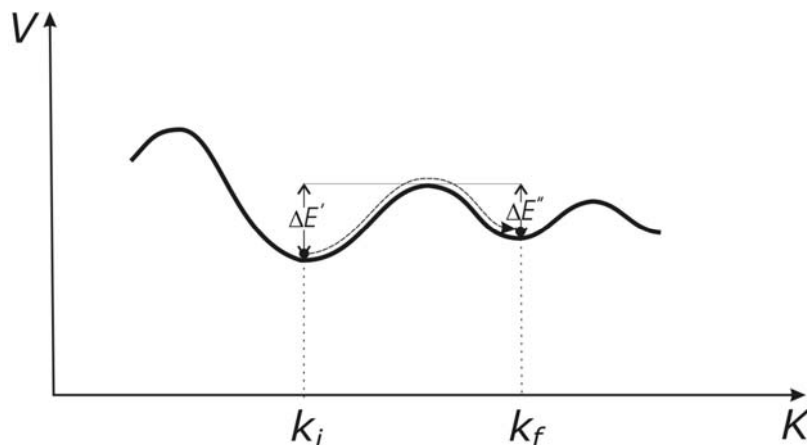


Fig. 2.4 The molecular electronic energy as a potential energy for the adiabatically decoupled (vibrational and) one-dimensional conformational system  $K$ .

The horizontal axis refers (for simplicity) to the „position“ of one-dimensional „particle“  $K$  - the configuration space of the system. The vertical axis refers to the conformational molecular electronic energy,  $V(k)$ , as a potential energy for the adiabatically decoupled (vibrational and) one-dimensional conformational system  $K$ ,  $k$  representing a value of the variable  $K$ . The local minima represent the (meta)stable conformations of a molecule with the following characteristic: the (one-dimensional) particle sitting in vicinity of a local minimum is attracted towards the minimum, finally centering around the bottom of the minimum (of a stable conformation). As a consequence, not every geometrically possible conformation may be taken by a molecule. Rather, only the conformations referring to the energetically preferable shapes are allowed - as defined by the local minima in Fig. 2.4. Certainly, the *continuous* change of shape of the molecule follows the  $V(k)$  plot in  $K$ -space. Once centered around the bottom of a local minimum, the particle does not have energy enough to change its position - *unless it's externally forced* to do so.

Therefore, the conformational change of a molecule can be (semi-)classically viewed as the continuous change of its geometrical shape originating from some initial  $k_i$  to the final conformation  $k_f$  (in two-conformational example of Fig. 2.4). Being in vicinity of a local minimum, the one-dimensional particle presented in Fig. 2.4 will tend to reach the minimum. This (semi-)classical model gives a background for the experimentally verified findings about the large molecules conformations. Unfortunately, it immediately gives rise to the problem - the so-called Levinthal's paradox [5].

Actually, as Levinthal emphasizes, the conformational transitions can be realized through a *sequence* of local rotations (cf. Fig. 2.3) eventually giving rise to another (energetically preferable) conformation. The *core of the Levinthal's paradox* can be presented as follows:

*For certain large molecules, the number of the local rotations necessary for effecting the conformational change (e.g.  $k_i \rightarrow k_f$  in Fig. 2.4) may be so large that the effective time necessary for completing the transformation becomes unreasonably long, thus making the whole procedure physically unrealistic a process.*

More precisely: Assuming  $2n$  torsional angles of a  $n$ -residue protein, each having three stable rotational states, this yields  $3^{2n} \approx 10^n$  possible conformations for the chain (even with rather gross underestimating). If a protein can explore new conformations in a *random way*, at the rate that single bond can rotate, it can find approximately  $10^{13}$  conformations per seconds, which is here an overestimating. We can then calculate the time  $t$ (s) required for a protein to explore all the conformations available to it:  $t = 10^n/10^{13}$ . For a rather small protein of  $n = 100$  residues, one obtains  $t = 10^{87}$  s, which is immensely more than the apparent age of the universe ("Levinthal paradox"). Yet, according to some experiments, proteins can fold to their native conformation in less than a few seconds [8]. It follows that conformational changes of proteins in solution, due to compositional, thermal, and other influences of the environment does not occur in a random way (as e.g. movements of gas particles) - but fold to their native conformation in some sort of *ordered set of pathways* in which the approach to the native state is accompanied by sharp increasing conformational stability - this being one of the most crucial questions in all life sciences.

The Levinthal's paradox raised the search for the preferred (ordered set of) pathways in  $K$ -space. The core of the research work in this regard refers to this task essentially pointed out by Levinthal. However, some recent approaches shed some new light in this concern.

## 2.4 Levinthal's paradox: Revisited

The new approach [6] (and references therein) goes beyond the concept of the preferred pathways. Actually, it refers to the details in the single molecule's conformational transitions yet searching for the fast transitions.

The approach calls for the specific *funnel*-structure of the more realistic multidimensional  $V(k)$ -hypersurface, that might provide the basis for fast conformational transitions. Actually, existence of the local *funnel-like* regions in  $V(k)$ -hypersurface is assumed, with the following main idea: The funnel-like shape *restricts* the set of the allowed trajectories (pathways) for the conformational change. The different trajectories should be stochastically taken by the different (single) molecules in the ensemble of molecules from the set of the possible trajectories in the *restricted K-space*.

Essentially, this proposal relaxes the original idea about the preferred pathways, yet in an elaborate fashion. Unfortunately, this is still a *qualitative* (semi-)classical model requiring much research work yet to be done; it is therefore hard to predict the success of this approach. E.g., one may notice that this proposal does not substantially go beyond the standard "pathways" (semi-)classical approach to the issue, especially in its *kinematical* context<sup>1</sup>.

## 3. NEW APPROACH: THE CLUE

The Levinthal's paradox emerges from the (semi-)classical picture of the molecules conformations defined in the  $K$ -space of the one-dimensional model of Fig. 2.4. Within this strategy, the particle bears a definite position  $k_i$  in every instant of time. Thus every conformational change can be represented by a „trajectory“ (path) in  $K$ -space, following the shape of  $V(k)$ .

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<sup>1</sup> The funnel-approach restricts the number of the possible pathways. Kinematically, it means that for  $n$  local rotations - no matter which path down the funnel has been taken by the molecule - there appears the constraint of *small n*. This constraint comes from the spectroscopic data on the poorly dimensionally-sensitive dispersion laws of the internal quasiparticle excitations [9,10], which stem the same order of magnitude for the two time intervals, for the molecular conformational transition ( $\tau$ ), as well as for the (average) time of the local segmental rotations ( $\tau_i$ ), while bearing  $\tau = n\tau_i$  in mind. Certainly, this might be a serious restriction, in principal, for the large molecules conformational transitions in the still (semi-)classical funnel approach.

Bearing this in mind, we speculate about the possible solution of the problem in the context of the following idea:

*To find the theoretical background allowing us to abandon the concept of the trajectory (the path)“ in  $K$ -space,*

in order to avoid the problems of the *kinematical nature*. Fortunately enough, there is a theory justifying this idea - quantum mechanics. Actually, in the full quantum-mechanical treatment, the one-dimensional particle  $K$  might be allowed the linear superpositions of the different „positions“, thus making the concept of the position (and consequently of „trajectory“) physically meaningless<sup>2</sup>.

*Prima facie*, this approach may seem un-reasonable, since it should simultaneously provide both existence as well as maintenance of the (stable) conformations in the stationary state of the system, *and* the model for fast conformational transitions. Fortunately enough, there is a quantum-mechanical theory meeting these criteria/requirements - the so-called *decoherence theory* [7]. Section 5 justifies this claim. In Section 4, we outline the fundamentals of the decoherence theory.

Finally to this section, we answer the following question:

*Why should one believe in quantum-mechanical behaviour of the large molecules? After all, the (semi-)classical approach seems perfectly to work for most purposes in chemistry.*

Our answer can be given in few steps.

*First*, the molecules are ultimately quantum-mechanical systems. It is therefore *per se* interesting to investigate this approach to the issue. *Second*, the „border-line“ between the „quantum“ and „classical“ is a matter of extensive research science-wide [7]. Particularly, it means that experience with the (semi-)classical behaviour does not necessarily remove the possibility of purely quantum-mechanical behavior of the large molecules. *Third*, the recent experiments on the macromolecules (spatial) interferometry [11,12] directly addresses the following question: Under *which circumstances*, one may expect the quantum-mechanical behaviour of the *mesoscopic* systems, with the view to even much larger („macroscopic“) systems? To this end, the lesson is rather simple: Rejecting the quantum-mechanical behavior of large molecules is just a matter of *stipulation*, not yet a scientific truth - as much as we know to date. *Fourth*, there is a quantum-mechanical basis for the macromolecules *individuality* in a liquid (solution), thus giving rise to the (seemingly) (semi-)classical basis of the kinetic theory<sup>3</sup> [13].

Therefore, we conclude:

*The macromolecules dynamics in a solution is an interplay between the different (even mutually competing) processes that are only poorly known to date, some of them bearing quantum-mechanical origin.*

## 4. THE FUNDAMENTALS OF THE DECOHERENCE THEORY

### 4.1 Terminology

A word of caution is worth saying. Sometimes, some physically different processes/effects are mis-identified/mis-interpreted as „decoherence“. Below, we give precise definition of decoherence - i.e. of the *decoherence-induced superselection rules effect* [14], which we refer to as „decoherence“.

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<sup>2</sup> To this end, one may use an analogy. E.g. in the interference experiments in optics, the concept of trajectory (of a particle traversing a slit in the diffraction grating) becomes meaningless - existence of trajectories vipes out the interference (diffraction) pattern on the screen. Interference is analogous to the coherent (quantum-mechanical) superpositions of the different “positions” in  $K$ -space.

<sup>3</sup> The individuality refers to distinguishing the particles in a liquid not yet compromising their quantum-mechanical behavior.

## 4.2 Open quantum systems

Standard quantum-mechanical theory deals with the *isolated* quantum systems, whose dynamics is governed by Schrodinger equation. For such systems, the environment effectively plays the role of the external potential, which is an additive term of the system's Hamiltonian. Needless to say, such dynamics is exactly reversible. On the other side, if the environment nontrivially acts on the system, such a system is referred to as the *open* quantum system: the interaction between the (open) system ( $S$ ) and its environment ( $E$ ) changes also the state of the environment, thus effecting irreversibly dynamics of the system  $S$ .

The open system's dynamics is crucially determined by the interaction in the composite system  $S + E$ . Usually, for the composite system  $S + E$ , one adopts validity of the Schrodinger equation. Then, the task is properly to describe the open system's dynamics. Probably the best known examples of open systems are: The object of quantum measurement; A quantum particle in Wilson chamber; Detection of a quantum particle on the screen.

From the mathematical point of view, the distinction between the isolated and the open systems can be described as follows:

(A) For the isolated systems, the effect of its environment is encapsulated by the „external potential“ (potential energy) of the particle,  $\hat{V}(\hat{x}_{Si}, \hat{p}_{Si}; a_{Sj}, A_{Ek})$ ;  $\hat{x}_{Si}, \hat{p}_{Si}$  denote the system's degrees of freedom as well as their conjugate momenta, while  $a_{Sj}, A_{Ek}$  represent the system's and the environment's parameters (such as the mass, electric charge, etc.), respectively. Needless to say,  $\hat{V}$  is the „one-particle“ observable changing the states of the open system, not yet of the environment.

(B) The interaction Hamiltonian  $\hat{H}_{S+E} \equiv \hat{H}_{\text{int}}$  is a two-body observable, coupling the observables of both the system  $S$  and environment  $E$ . The composite system's Hamiltonian reads:

$$\hat{H} = \hat{H}_S \otimes \hat{I}_E + \hat{I}_S \otimes \hat{H}_E + \hat{H}_{\text{int}}, \quad (4.1)$$

where the third term denotes the interaction energy, which is a „two-system“ observable changing, in general, the states of both  $S$  and  $E$ .

## 4.3 The task

The central issue of quantum mechanics of open systems is calculating the open system's dynamics. Let us by  $\hat{\rho}_S(t=0)$  denote the open system's initial state, while by  $\hat{\sigma}_E(t=0)$  we denote the initial state of the environment. Then, by definition, the initial state of the composite systems  $S + E$  reads:

$$\hat{\rho}_S(t=0) \otimes \hat{\sigma}_E(t=0). \quad (4.2)$$

Then (4.1) gives uniquely rise to the unitary evolution operator  $\hat{U}$  for the composite system, i.e. to the unitary dynamics of the composite system:

$$\hat{\rho}_{S+E}(t) = \hat{U} \hat{\rho}_S(t=0) \otimes \hat{\sigma}_E(t=0) \hat{U}^*. \quad (4.3)$$

Now, according to the general rules of quantum mechanics, the subsystem's state is defined as:

$$\hat{\rho}_S(t) = \text{tr}_E \hat{\rho}_{S+E}(t), \quad (4.4)$$

with „ $\text{tr}_E$ “ denoting the „tracing out“ (integrating over) the environmental degrees of freedom.

It is apparent that the interaction term  $\hat{H}_{\text{int}}$  is central to the open system's dynamics. E.g., if one may write (in accordance with the above (A)):

$$\hat{H}_{\text{int}} = \hat{V}_S \otimes \hat{I}_E + \hat{I}_S \otimes \hat{V}'_E, \quad (4.5)$$

then the two subsystems evolve mutually independently in time:

$$\hat{\rho}_{S+E}(t) = \hat{\rho}_S(t) \otimes \hat{\sigma}_E(t). \quad (4.6)$$

However, for the non-trivial coupling of the observables of the two subsystems, one obtains (cf. the above point (B)) the correlations of states of the subsystems.

As to the decoherence theory, the most interesting is the situation in which the initial state of the system  $S$  is a „pure“ quantum state (an element of the system’s Hilbert state space),  $|\psi\rangle_S$ :

$$\widehat{\rho}_S(t=0) = |\psi\rangle_S \langle\psi|. \quad (4.7)$$

Writing

$$|\psi\rangle_S = \sum_i C_i |\varphi_i\rangle_S, \quad (4.8)$$

one may directly obtain:

$$\widehat{\rho}_S(t=0) = \sum_{i,j} C_i C_j^* |\varphi_i\rangle_S \langle\varphi_j|. \quad (4.9)$$

with the non-zero off-diagonal ( $i \neq j$ ) terms of  $\widehat{\rho}_S$ .

One of the central findings of the decoherence theory is the observation that for certain special states (orthonormalized basis)  $\{|\varphi_i\rangle_S\}$ , the evolution in time effects in the loss of the off-diagonal terms of  $\widehat{\rho}_S$ . That is, one may write for the off-diagonal terms of  $\widehat{\rho}_S$ :

$$\lim_{t \rightarrow \infty} \rho_{Sij}(t) = 0, i \neq j \quad (4.10)$$

for the rather *short time intervals* of the order of  $\tau_D$  -the decoherence time.

More precisely: The matrix representation of  $\widehat{\rho}_S$  in the basis  $\{|\varphi_i\rangle_S\}$  - the „pointer basis“ - is of the quasi-diagonal form, thus giving rise to the *effective superselection rules* [14,15] for the open system that is described by the orthogonal decomposition of the system’s Hilbert state:

$$H_S = \sum_n^{\oplus} H_n. \quad (4.11)$$

Physically, the environment influences the loss of coherence in the open system’s state,  $H$ , for the states belonging to the different subspaces  $H_n$ ;  $\langle\varphi_i|\varphi_j\rangle = 0$ , if  $|\varphi_i\rangle \in H_n, |\varphi_j\rangle \in H_{n'}, n \neq n'$ .

#### 4.4 The environment-induced decoherence

The loss of the initial coherence can be presented as follows:

$$\sum_{i,j} C_i C_j^* |\varphi_i\rangle_S \langle\varphi_j| \xrightarrow{\tau_D} \sum_i |C_i|^2 |\varphi_i\rangle_S \langle\varphi_i|, \quad (4.12)..$$

meaning that coherence between the states belonging to the different subspaces,  $H_n$ , is effectively forbidden after the (rather *very short* [7,15]) time interval of the order of the decoherence time.

Alternatively, the decoherence effect can be described by the *existence* of the „pointer observable“,  $\widehat{\Lambda}_S$ , whose spectral form reads [14,15]:

$$\widehat{\Lambda}_S = \sum_n \lambda_n \widehat{P}_{S_n}, \quad (4.13)$$

where the projectors  $\widehat{P}_{S_n}$  are in one-to-one correspondence with the subspaces  $H_n$  (appearing in (4.11)). This observable is the center of algebra of the observables of the open system  $S$ , while fulfilling the commutator relation [14-16]:

$$[\widehat{H}_{\text{int}}, \widehat{\Lambda}_S \otimes \widehat{I}_E] = 0. \quad (4.14)$$

#### 4.5 The physical contents

The decoherence effect is a striking effect: Effectively, there is the loss of coherence in the open system’s state space. This restricts both the states and the observables of the open system that can be observed by an independent observer [7].

The lack of coherence is exactly what is expected from a *macroscopic* (a classical) system, which is subject to the classical *determinism* and *reality*. Actually, for the macroscopic systems, one may say that coherent superpositions of the type (4.8) have never been observed. Paradigmatic in



this concern are the macroscopic „center-of-mass“ coordinates of a macroscopic body/object. This is the reason the decoherence effect is sometimes considered as the main candidate for finding out the solution to the problem of the transition from „quantum to classical“ [7,15]. To this end, the „pointer basis“ as well as the „pointer observable“ are considered to bear the macroscopic characteristics of an open quantum system.

Also crucial is the following observation: *relative to*  $\widehat{H}_{\text{int}}$ , the elements of a „pointer basis“ (which is also an eigenbasis of  $\widehat{\Lambda}_S$ ) are *robust* [15,16]. Physically, it means that, once effected, the decoherence will keep the states of a „pointer basis“ effectively intact in the course of the unitary evolution of the composite system  $S + E$ . This robustness of certain system's states is crucial for the macroscopic context of the decoherence theory. Particularly, it means that the decoherence effect gives rise to both, *existence* as well as to *maintenance* of states of a „pointer basis“ - i.e. the relevance of the superselection rules - of an open system in the course of the unitary evolution of the combined system  $S + E$ . In other words, the decoherence effect tends to freeze the open system's dynamics as defined by the decomposition (4.11). The decoherence time  $\tau_D$  is usually very short, including the *mesoscopic systems* such as certain macromolecules [12]. It is therefore not for surprise that the decoherence effect has been observed in the quite controlled circumstances only recently [12,17,18].

Finally, in principle, certain *external actions* on the composite system can effect in breaking the superselection rules, i.e. of the decoherence effect. Actually, for certain interactions with another external system  $E'$ , if one may write:

$$\left[ \widehat{H}'_{\text{int}}, \widehat{\Lambda}_S \otimes \widehat{I}_E \right] \neq 0, \quad (4.15)$$

there might appear the coherent superpositions of states from the pointer basis. E.g., if  $\widehat{H}'_{\text{int}}$  is such that: (i) it dominates in the system, and (ii) it defines another decomposition in contradistinction with (4.11), then one may obtain another „pointer basis“,  $\{|\chi_i\rangle_S\}$ , such that:

$$|\chi_j\rangle_S = \sum_i d_{ij} |\varphi_i\rangle_S. \quad (4.16)$$

In the macroscopic considerations, the possibility of such an effect is generally neglected. However, this need not be the case for the *mesoscopic systems*, such as the macromolecules.

## 5. NEW APPROACH

Formally, we deal with the one dimensional system ( $S$ ),  $(\widehat{K}_S, \widehat{P}_S)$ , where  $\widehat{K}_S$  stands for the „coordinate“ *conformation*, while the momentum  $\widehat{P}_S$  satisfies:

$$\left[ \widehat{K}_S, \widehat{P}_S \right] = ih / 2\pi. \quad (5.1)$$

However, the system  $S$  is an *open system* - as distinguished in Section 2. It unavoidably interacts with its environment, which physically consists of the (liquid's) molecules. Therefore, the system of interest is the composite system „conformation + liquid (S+E)“.

In this section, we address the following tasks:

- (a) To establish existence *and* maintenance of an ensemble of conformations in the *stationary state* of the composite system, where the conformations  $|k_i\rangle_S$  satisfy:

$$\widehat{K}_S |k_i\rangle_S = k_i |k_i\rangle_S; \quad (5.2)$$

- (b) To model the conformation change,  $|k_i\rangle_S \rightarrow |k_f\rangle_S$ , from the set of the allowed conformations.

Physically, the task (b) refers to the *non-stationary state* of the composite system that is induced by the external action (point (ii) of Section 2.2). *Prima facie*, these two tasks might seem formidable. Fortunately enough, there is a quantum-mechanical theory fulfilling these tasks - the decoherence theory.

## 5.1 The conformation stability

The composite system  $S + E$  is formally defined by the Hamiltonian of the form (4.1). For simplicity, we shall further deal exclusively with the interaction term,  $\widehat{H}_{S+E} \equiv \widehat{H}_{\text{int}}$ .

As we learned from Section 4: A proper choice (model) of  $\widehat{H}_{\text{int}}$  might provide both existence and stability of an ensemble of conformations in the stationary state of the composite system. To this end, it is crucial to recognize the conformation  $\widehat{K}_S$  as the “pointer observable” of the system. In an ensemble of conformations, in general, every conformation,  $|k_i\rangle_S$ , should be ascribed a probability  $p_i$ ;  $\sum_i p_i = 1$ . Then, the initial stationary state (point (i) of Section 2.2) of the ensemble is described by the statistical operator:

$$\widehat{\rho}_S = \sum_i p_i |k_i\rangle_S \langle k_i|. \quad (5.3)$$

More precisely, in order to obtain existence (appearance *due to decoherence*) and maintenance (stability *due to decoherence*) of the conformations in the initial state (5.3), it is necessary (and for certain simple models, it is sufficient) to have satisfied the condition/requirement [16]:

$$[\widehat{H}_{\text{int}}, \widehat{K}_S \otimes \widehat{I}_E] = 0. \quad (5.4)$$

Fortunately enough, this gives rise to applicability of a rather wide class (and types) of the interaction Hamiltonians.

Actually, one may write (for the time independent interaction) for the unitary operator of the composite system:

$$\widehat{U} \cong \widehat{U}_{\text{int}} = \exp\{-ith\widehat{H}_{\text{int}}/2\pi\}, \quad (5.5)$$

which for the initial state (*before* the „initial stationary state“ (5.3))

$$|\psi(t=0)\rangle = \sum_i C_i |k_i\rangle_S \otimes |0\rangle_E, \quad (5.6)$$

gives for the state in an instant  $t$ :

$$|\psi(t)\rangle = \sum_i C_i |k_i\rangle_S \otimes |\chi_i(t)\rangle_E, \quad (5.7)$$

satisfying the condition:

$$\lim_{t \rightarrow \infty} |\langle \chi_i(t) | \chi_j(t) \rangle| = 0, \quad i \neq j. \quad (5.8)$$

Needless to say, then one obtains satisfiability of the condition (4.10) - existence (appearance) of the preferred states of the open system  $S$ , the set of preferred conformations. Since (5.4) guarantees stability (robustness) of the conformations, relative to  $\widehat{H}_{\text{int}}$ , the requirement of maintenance of the conformations is also satisfied, where  $p_i = |C_i|^2$ . Physically: The proper model (5.4) gives rise to appearance and stability of conformation for every single molecule in the liquid in the initial stationary state (5.3).

## 5.2 Nonstationary state

The external action on the composite system (point (ii) of Section 2.2) gives rise to the change of the system’s parameters. It is the fact: Such external actions might induce the change of the stationary state as well as of the conformational transitions for every single molecule. In effect, there appear another ensemble of the possible conformations.

Modeling the non-stationary state in the general terms is rather simple. Actually, it seems quite natural to assume that the external action *changes the interaction* in the composite system. Furthermore, it is certainly the case that the new (effective) environment,  $E'$ , appears. Therefore, one should assume the new interaction term,  $\widehat{H}_{S+E'} \equiv \widehat{H}'_{\text{int}}$ . Setting (cf. (4.15)):

$$[\widehat{H}'_{\text{int}}, \widehat{K}_S \otimes \widehat{I}_{E'}] \neq 0, \quad (5.9)$$

and consequently  $[\widehat{H}'_{\text{int}}, \widehat{H}'_{\text{int}}] \neq 0$ , one may obtain the change of conformations.

Assuming that the external action is so strong that  $\widehat{H}'_{\text{int}}$  *dominates* in the system, then the spectral form (5.3) necessarily changes. Actually, then one may write:

$$[\widehat{\rho}'_S, \widehat{\rho}'_S] \neq 0, \quad (5.10)$$

where the state  $\widehat{\rho}'_S$  refers to the nonstationary state, and is defined as:

$$\widehat{\rho}'_S(t) = \text{tr}_E \widehat{U}'_{\text{int}} \widehat{\rho}_{S+E'}(t') \widehat{U}'_{\text{int}}{}^*, \quad t > t'; \quad (5.11)$$

where  $\widehat{U}'_{\text{int}} = \exp\{-ith\widehat{H}'_{\text{int}}/2\pi\}$ .

These general considerations do not restrict significantly the possible set of states  $\widehat{\rho}'_S(t)$ . Furthermore, due to (5.10), one may be free to write:

$$\widehat{\rho}'_S(t) = \sum_i \pi_i(t) |\chi_{it}\rangle_S \langle \chi_{it}|, \quad (5.12)$$

where, in general, there *appears coherence of the different conformations*:

$$|\chi_{it}\rangle = \sum_i \alpha_{ij} |k_i\rangle_S. \quad (5.13)$$

Physically, the external action breaks the initial loss of coherence, which is caused by decoherence giving rise to the initial stationary state (5.3). This observation is virtually totally independent on the assumptions about the new interaction (in the system  $S + E'$ ) [16].

The non-stationary state is expected to be terminated by the relaxation process.

### 5.3 The relaxation process

Following the evidence (point (iii) of Section 2.2), we assume that the external action terminates, eventually giving rise to the relaxation process. Actually, we assume that the relaxation process gives rise to *re-establishing* of the stationary state, which, in turn, should be determined by the *same kind* of interaction - selecting the conformational states as the „pointer basis“. Actually, we assume that the new composite system,  $S + E'$ , is defined by the interaction of the *kind*<sup>4</sup> (5.4). With this *natural assumption*, we easily reproduce re-appearance of conformations, as the final states for every single molecule - cf. Section 4.

Namely, validity of (5.4) in the final stationary state gives rise to the possible *occurrence of decoherence* in the composite system  $S + E'$ . This is exactly what we have required in Section 2: Essentially, the stationary states (initial and final ones) should qualitatively coincide - being characterized by the appearance and stability of conformations.

Formally, if we denote the final state (after the relaxation process) by  $\widehat{\rho}''$ , then the relaxation process gives rise to the transition:

$$\widehat{\rho}'_S \xrightarrow{\text{relaxation}} \widehat{\rho}''_S, \quad (5.14)$$

while the subsequent decoherence gives rise to:

$$\widehat{\rho}''_S \xrightarrow{\text{decoherence in the new stationary state}} \widehat{\rho}'''_S. \quad (5.15)$$

The point strongly to be emphasized is that  $\widehat{\rho}'''_S$  now reads, in general as:

$$\widehat{\rho}'''_S = \sum_j q_j |k'_j\rangle_S \langle k'_j|, \quad (5.16)$$

<sup>4</sup> Not necessarily of the same type (of the same form).

where, in general, appear both the different conformations<sup>5</sup>,  $|k'_j\rangle_S$ , as well as the *different probabilities*  $q_j$  (of the possible conformations in the final ensemble) than in the initial stationary state (5.3).

Needless to say, physically, this means that the *net effect* is the conformational change:

$$\hat{\rho}_S = \sum_i p_i |k_i\rangle_S \langle k_i| \rightarrow \hat{\rho}^m_S = \sum_j q_j |k'_j\rangle_S \langle k'_j|, \quad (5.17)$$

as it is experimentally observed.

## 5.4 The model

We keep in mind the requirements of Section 2. Then, with respect to the experience with the decoherence theory (Section 4), we call for the rather general, hopefully *realistic assumptions* about the composite system, i.e. about the interactions in the composite system(s) - (5.4) and (5.9).

Concretely, we assume:

- (A) Every *stationary state* (initial, intermediate-if such exist-states, as well as the final one) is characterized by interaction in the composite system that is of the *same kind* - being able to give rise to the occurrence of decoherence with the conformations as the “pointer basis states”.
- (B) Non-stationary state is characterized by the *change in the character of interaction* in the composite system.

The net effect takes the following „phases“, each having its own characteristic time:

- (a) External action (producing the non-stationary state), taking time  $T_{ext}$ ,
- (b) Relaxation process (establishing the new, final stationary state), taking time  $T_{relax}$ ,
- (c) Decoherence process (*in the final stationary state*), taking time of the „decoherence time“,  $\tau_D$ .

Therefore, to summarise, the conformation transition (5.17) *takes time*:

$$T_{ext} + T_{relax} + \tau_D \quad (5.18)$$

which (cf. Section 4) gives (plausibly) rise to

$$T_{ext} + T_{relax} + \tau_D \approx T_{ext} + T_{relax} \quad (5.19)$$

Therefore, we conclude:

*In our model, the Levinthal's paradox completely disappears.*

## 6. DISCUSSION

We essentially make a couple of plausible assumptions/interpretations of the phenomenological data which allow the natural accounting for the decoherence effect in the composite system „conformation + environment“. These assumptions are worth repeating. First, we assume that every stationary state of the composite system - that is characterized by the constant values of the system's parameters - is characterized by the same *kind* of interaction in the composite system (cf. (5.4)). Second, we assume that the external action - eventually giving rise to the conformational transitions - substantially change the kind of interaction in the (new) composite system (cf. (5.9)). It is a matter of the general decoherence theory straightforwardly to prove the final result (5.17), as well as (5.19) [7,14-16,19].

Needless to say, the system  $S$  (the „conformation“) is (likewise in the (semi-)classical approach) a characteristic of a (single) molecule as a *whole*. That is, as usual, we do not take into account the local details of the conformational rotations themselves, which essentially take into account the electron state transitions. As much as we can see, these are of the secondary importance

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<sup>5</sup> An extreme case is  $|k_i\rangle = |k'_j\rangle$ , while  $p_i \neq q_j$ . This is just the change of concentrations of the initial conformations.

to our model, which abandons the concept of the transitions in  $K$ -space. Abandoning the  $K$ -space is key to the possible success of our model: It is a decoherence-like process that breaks stability of conformations (in the non-stationary state), eventually giving rise to the possibility of rather fast conformational transitions.

There is the following prediction from our model: Even for the single (unique) initial conformation in the composite system ( $p_0=1, p_i=0, \forall i \neq 0$  - cf. (5.3)), our model *predicts* appearance of a *set* (non-unique) of the *final conformations* ( $q_j \neq 1, \forall j$  - cf. (5.16)). Distinguishing experimentally between this prediction and the opposite possibility - e.g. one-to-one conformational transitions - might sharpen the role of our proposal in the context of the conformational transitions problem.

Bearing in mind the foundations of the decoherence process, it should be also stressed: A definition of an open system goes *simultaneously* with defining the system's environment [20,21]. A strong, local interaction with a part of the environment may redefine the open system, simultaneously defining the rest of the environment as the new environment for the new open system. This way, even the larger „pieces“ of a living cell may be allowed the quantum-mechanical behavior - which, we believe, might be of interest in the biomolecular recognition process [22,23].

## 7. CONCLUSION

The Levinthal's paradox is an open problem yet. In order to avoid the *core* of the problem - it's *kinematical* aspect - we propose a new approach in this regard. Actually, we treat the macromolecules conformations as the quantum-mechanical observable. Bearing in mind the foundations of the decoherence theory, we are able to model both, existence and maintenance of the conformations *as well as* the conformational transitions in the *rather short* time intervals. Our model is rather qualitative yet a general one, while completely removing the Levinthal's paradox - in contradistinction with the (semi-)classical approach to the issue.

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