A Unified Decoherence-Based Model of Microparticles in a Solution

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Abstract. The complex behavior of microparticles in a solution calls for different theoretical backgrounds. Here, we follow the line of two, recently developed theories on individuality, on the one hand, and conformational transitions of macromolecules in a solution, on the other. Given as separate theories, the two models may raise certain controversy in respect to their mutual consistency. Needless to say, their mutual consistency is necessary for the validity of the theories both in a general context as well as in search for a unified physico/chemical picture concerning the microparticles in a solution dynamics. We point out the consistency of these theories based on the definition of a molecule through its constituent subsystems (e.g. the center-of-mass and the "conformation" subsystems).

Introduction

Complex behavior of microparticles (atoms, ions, molecules, and especially of macromolecules, e.g. biomolecules) in a solution raises certain fundamental physical questions and problems. For example, the kinetic theory assumes certain *individuality* of microparticles in a solution [1,2]. On the other hand, the (phenomenological) sudden conformational transitions for macromolecules raise a problem that is fairly presented by the profound Levinthal's paradox [3]. To this end, recently, some progress based on quantum mechanics of open systems (and particularly on the so-called *decoherence theory*) has been made [4-6]. Nevertheless, these results may, *prima facie*, seem mutually inconsistent. In other words: the theories expounded in [4] and in [5,6] bear certain subtlety that requires additional clarification – which is the subject of the present paper.

The microparticles individuality requires suppression of entanglement [1,2,4] (and consequently of decoherence [7]), which, in turn, may seem inconsistent with the decoherence-based model for macromolecules conformational transitions [5,6]. Therefore, making these theories mutually consistent is a condition for their physical relevance in the general context. In other words: mutual inconsistency of the theories might mean physical nonvalidity of at least one of the theories.

In this paper, we point out mutual consistency of the aforementioned theories, and offer a broader physical picture of the microparticles in a solution as well.

Microparticles as Open Quantum Systems

Microparticles (atoms, ions, (macro)molecules) are usually found in a solution. A wealth of physical effects for microparticles is therefore assumed somehow to be *induced by the environment*- the *open* systems dynamics, i.e. by interaction of the solution molecules with the microparticles.

Certain effects (e.g. the diffusion-based effects) can be (semi)classically [8] described by proper kinetic equations (or more generally by master equations). To this end, the basic assumption is individuality of microparticles, i.e. the possibility of treating a microparticle as a system bearing a definite quantum state. However, this assumption seems unjustified by quantum mechanics of open systems - as one would expect appearance of quantum entanglement in the composite system "microparticle + solution molecules" [1]. In order to resolve this seemingly contradictory situation,

a model for suppressing entanglement (and consequently of decoherence [7]) has been proposed [4], cf. Appendix A.

On the other hand, the problem with the (macro)molecules conformational transitions - the so-called Levinthal's paradox [3] - has been circumvented in a model based on the decoherence effect [5,6], cf. Appendix B.

Altogether, our theories assume simultaneous non-occurrence [4] and occurrence of decoherence [5,6] for the same ensemble of microparticles in a solution. *Prima facie*, this might seem contradictory.

This notion remains relevant even for the molecules usually not found in the definite conformations ("orientation" - e.g. chirality [9]), such as e.g. the ammonia molecule, which is usually found in the energy eigenstates (the definite energy states) [10]. Nevertheless, the answer to this kind of situation, again, is decoherence [10]: the energy eigenstates are selected by the decoherence process itself.

One way or another, the main problem seems generally to persist: for certain purposes, decoherence should be avoided, while for the other, decoherence seems to set a basis for the possible final solution of the problem at issue.

The Decoherence Models

One may wonder why, after all, one would expect the "mixed" - quantum mechanical and/or a (semi)classical-behavior - of microparticles in a solution. However it may be, a broader physical picture is desirable. In this section, we answer this question and offer a basis for a broader (unified) picture for the microparticles in a solution.

Why Quantum?

All microparticles are genuinely quantum mechanical objects. It is therefore natural to expect that certain microparticles, in a certain situation, can exhibit some quantum mechanical behavior. The observation of such kind of effects for macromolecules [11,12] justifies this expectation, yet posing the question of observability of the quantum effects up to the macroscopic scale [13], thus reinforcing the fundamental problem of the "transition from quantum to classical" [14,15].

Why Classical?

The microparticles in a solution are truly the *open* (quantum) systems - i.e. the systems in unavoidable interaction with their environment (as emphasized in the next section). As the foundations of the decoherence theory set, such systems exhibit a strong preference for the effectively *classical* (semiclassical [8]) behavior [14,15]. This kind of behavior has been observed in the experiments conducted, e.g. by Brune et al. [16], Amann et al. [17], and Hackermuler et al. [18], thus promoting the decoherence effect as the main candidate for the solution of the problem of the "transition from quantum to classical" [14,15].

Towards a unified picture

The point to be emphasized is as follows: the models (theories) considered, [4] and [5,6], assume *different degrees of freedom* of a microparticle which are usually considered to be mutually dynamically decoupled. Actually, as we point out in the sequel, avoiding decoherence refers to the center-of-mass (*CM*) degrees of freedom, while the decoherence-based conformational transitions refer to the specific "relative" coordinates - the so-called "reaction (conformational)" coordinates - defining the molecule conformations (*K*).

A single-molecule *system of electrons and nuclei* (as well as any more-dimensional system) can be redefined by the proper canonical (linear) transformations of the form:

$$\{x_i, p_i; x_\alpha, p_\alpha\} \rightarrow \{X_{CMj}, \Pi_{CMj}; \xi_{\mathrm{rel}i}, \pi_{\mathrm{rel}i}; \xi_{\mathrm{rel}\alpha}, \pi_{\mathrm{rel}\alpha}\} \tag{1}$$

Where x_i and x_α denote the original (Descartes) respective electronic and nuclei degrees of freedom, X_{CMj} are the center-of-mass coordinates of the single-molecule nuclei system, and the relative

electronic and nuclei coordinates $\xi_{\text{rel}i}$ and $\xi_{\text{rel}\alpha}$ are defined as "internal" in respect to the *CM* coordinate system (while p_i, p_α, Π_{CMj}, $\pi_{\text{rel}i}$, $\pi_{\text{rel}\alpha}$ are the corresponding conjugate momenta). In order to describe the molecule's possible conformations (K), the reaction coordinates K_i can be formally introduced:

$$\{\xi_{\text{rel}\alpha}\} \rightarrow \{K_i\}, \tag{2}$$

as the transforms *exclusively* of the relative nuclei coordinates $\xi_{\text{rel}\alpha}$. It particularly means that the center-of-mass coordinates (and their conjugate momenta) remain *intact* by the coordinate transformations of Eq. (2). Physically, it means that the effective degrees of freedom of the two subsystems - of the center-of-mass system (*CM*) and of the conformation-system (*K,* defined by the reaction coordinates) - appear mutually completely dynamically decoupled. Quantum mechanically, this is really *sufficient condition* for the absence of entanglement of states of the two subsystems, *CM* and *K*. From the general quantum mechanical point of view, it follows that the two subsystems can be independently described thus bearing the definite states of their own; i.e. the state of the composite system is a direct product of states of the general form $\left|\chi\right\rangle_{CM} \otimes \left|\phi\right\rangle_K$.

Now, we want to stress: the model for the microparticles individuality [4] (cf. Appendix A) refers to the *CM* system, while the model for the conformational transitions [5,6] (cf. Appendix B) refers to the system *K* of the microparticle's electronic-vibrational subsystem. Bearing in mind Eqs. (1) and (2), it becomes clear that the maintaining individuality of the *CM* system does not interfere with the decoherence-based state transitions for the system *K*. Therefore, the two models are mutually consistent - which is probably not obvious from the general formulation of the models [4-6].

A Unified Picture

The mathematical form of the above given (unified) model can be presented by the Hamiltonian of the composite system "microparticle-system + environment". Actually, bearing in mind that a single microparticle (e.g. a macromolecule) contains the complex system *CM + K*, the total Hamiltonian of *CM + K+ E* can be presented as follows:

$$\widehat{H} = \widehat{H}_{CM0} + \widehat{H}_{K0} + \widehat{H}_{E0} + \widehat{H}_{CM+E_1} + \widehat{H}_{K+E_2} + \widehat{H}_{E_1+E_2}. \tag{3}$$

Hereby we assume for $\widehat{H}_{K0}$ the electronic-vibrational Hamiltonian, which includes operators of kinetic energies and all Coulomb interactions between the microparticle electrons and nuclei in the *CM* coordinate system; also, we assume that there is a general environment *E*, influencing the subsystems (*CM* and *K*) in different ways, i.e. different possible decoherence mechanisms: so, environment *E* is defined as $E = E_1 + E_2$, as elaborated in Appendix A. Needless to say, the consistency of the model requires non-interaction between *K* and E_1 - otherwise there appear the state correlations (entanglement) between *K* and E_1, in contradiction with the basic assumption of "freezing" the state of E_1 (cf. Appendix A). Now, it is apparent how subtle the (unified) model actually may be regarding the realistic physicochemical situations.

The emerging physical picture is as follows: for a comparatively long time interval, the microparticle's *CM* (sub)system maintains its individuality, while the solvent molecules force the microparticle to choose a definite - e.g. conformational state. This unifying picture refers to every single microparticle in a solution that involves the subsystems *CM* and *K* as defined above.

Needless to say, much remains yet to be investigated in order to describe properly the rich dynamics of an ensemble of microparticles in a solution. For certain open questions cf. next section.

Discussion

The basic assumption of our model (cf. Eq. (3)) is the approximation that the two systems, *CM* and *K*, may be considered to be mutually decoupled. In general, this need not be the case. So, in order to keep our unified model consistent with the phenomenology, we assume that the exact model of the

Hamiltonian $\hat{H}$ in Eq. (3) might bear the small terms describing (e.g. mediated) interaction of the two subsystems, *CM* and *K*, which are truly the subtleties that should be carefully investigated for a *concrete model* of the composite system *CM + K + E* that will not be elaborated here. The same applies to the degrees of freedom neglected in the model of Eq. (3).

Actually, the system *CM + K* does not describe the microparticle as a whole, because the microparticle (e.g. a macromolecule) system *S* should also include the energy term related to rotational degrees of freedom (*R*) of the microparticle as a whole: *S = CM + R + K*. The "external" degrees of freedom, *CM* and *R*, remain untouched by the transformations of Eq. (2), which defines the "internal" degrees of freedom, *K*. Needless to say, every coupling in the composite system *CM + R + K* may induce a mediated interaction between the systems *CM* and *K* - that thoroughly depends on the concrete system in a concrete physical situation and can hardly be described by fully general terms.

It is usually assumed that the kinetic- (or more general, the master-) equations formalism requires occurrence of decoherence as the fundamental quantum mechanical background [19]. Clearly, this assumption is not fulfilled by the model of Refs. [4,7]. However, this model offers a basis for *mimicking decoherence*, thus effectively defining the *CM* states as the well-defined, noninterfering states - in agreement with the foundations of the kinetic theory.

Actually, as it appears in Eq. (A.1) of Appendix A, the system *S* (i.e. the subsystem *CM*) evolves in time according to [4,7]:

$$\left|\Psi(t)\right\rangle_S = \sum_i C_i \exp\{-it(\,_S\langle i|\hat{H}_{S0}|i\rangle_S + \,_{SE_1}\langle i0|\hat{H}_{SE_1}|i0\rangle_{SE_1}\,)/\hbar\,\}|i\rangle_S = \sum_i C_i \exp\{-i\delta_i t\}|i\rangle_S \qquad (4)$$

The appearance of the time-dependent phase in Eq. (4) may give rise to *the effective loss of coherence* (of the states $|i\rangle_S$): while the off-diagonal terms do not disappear themselves, their *time averages* do disappear [20]. So, for the comparatively strong interaction $\hat{H}_{SE_1}$, the fast oscillation of the off-diagonal elements mimics the decoherence effect. This loss of coherence for an *isolated* system - the so-called dephasing effect - mimics the decoherence-induced loss of coherence, and is sometimes misinterpreted as the decoherence effect itself. Physically, the loss of coherence gives rise to the well-defined states of the (quasi)isolated system *CM*, thus setting a consistent basis for the kinetic theory, and additionally justifying the unified picture of the previous section.

Finally, it is worth stressing: a decomposition of the system *S* into subsystems is in accordance with the foundations of the decoherence theory [21]. This, however, tackles the truly fundamental problem of "what is system" (cf. e.g. Refs. [14,22-24]).

Conclusion

The phenomenology of the microparticles in a solution sets the specific theoretical requirements. Here, we follow the line of two, recently developed theories on the individuality, on the one hand, and the conformational transitions of the microparticles in a solution, on the other. We point out consistency of these theories thus probably justifying their relevance in a wider context of the microparticles (atoms, ions, molecules) in a solution.

Acknowledgement

Appendix A

Avoiding decoherence for an open system [7] assumes the entanglement suppression [4]. This goal can be fulfilled for a composite (tripartite) system, $S + E_1 + E_2$, by specific assumptions, cf. below. Physically, the idea is as follows: a proper *control* of the S's environment (E_1) by an external system (E_2) may give rise to the *"freezing"* of the state of E_1. And this is exactly the basis for the entanglement suppression, and consequently of the possibility to avoid decoherence for the open system S.

Actually, the following assumptions should be fulfilled: (a) the interaction in the system $E_1 + E_2$, $\widehat{H}_{E_1E_2}$, dominates the composite system dynamics: (b) there exists a state $|0\rangle_{E_1}$ of E_1 that is "robust", relative to the interaction in the $E_1 + E_2$ system ($_{E_1}\langle 0|\widehat{H}_{E_1E_2}|i\rangle_{E_1} = 0$, for $_{E_1}\langle i|0\rangle_{E_1} = 0$); and (c) there is not interaction between S and E_2, $\widehat{H}_{SE_2} = 0$. Then, one may obtain the *exact* form of a pure state for the composite system $S + E_1 + E_2$ [7]:

$$|\Psi(t)\rangle_{SE_1E_2} = \sum_i C_i(t)\exp\{-it\lambda_{i0}^{(1)}/\hbar\}|i\rangle_S \otimes \exp\{-it\lambda_\circ/\hbar\}|0\rangle_{E_1}$$

$$\otimes (\sum_j \beta_j(t)\exp\{-it\lambda_{i0j}/\hbar\}|j\rangle_{E_2}) + |O(\varepsilon)\rangle_{SE_1E_2} \qquad (A.1)$$

where appears the small term $|O(\varepsilon)\rangle_{SE_1E_2}$, and the dominant term is calculated in accordance with the standard (time independent) perturbation theory. The small term ε is of the order of $|c/C| \ll 1$, c denotes the coupling constant for $\widehat{H}_{SE_1}$, and C for $\widehat{H}_{E_1E_2}$. (For more details cf. [4,7].)

From Eq. (A.1), it is obvious: for the time interval $\tau \ll (\sup\{\lambda_{i0j}\})^{-1}$, the dominant term exhibits the effectively unitary evolution in time of the open system S - which is the basic result of the model [4,7].

Originally, the model referred to the task of combating decoherence for a qubit, an elementary carrier of quantum information in quantum computation [7]. When applied to a microparticle in a solution, this model, *by its definition*, refers to the states $|i\rangle_{CM}$ of the subsystem *CM*, i.e. to the states defining the position of a microparticle in a solution: $|i\rangle_{CM} \equiv |\vec{R}\rangle_{CM}$.

Appendix B

The complex molecules conformational transitions are subject to the profound Levinthal paradox [3]. The paradox can be expressed in at least two ways. First, for the typical-molecule (conformational) transitions, it establishes a physically non-reasonably long time necessary for the transition to be completed. Second, in an ensemble of the molecules, it establishes a negligible fraction of the molecules that have completed the transition. In effect, such transitions are physically in-achievable.

Levinthal's paradox essentially assumes a *classical-physics* process - the successive local rotations. This is the reason that the *quantum paradigm might help* in this regard.

The model [5,6] of the decoherence-based conformational transitions bears the following assumptions: (a) in a stationary state of the system "molecule's conformation + solution" ($K + E_2$), the interaction between K and E_2 forces the occurrence of decoherence that selects the well-defined conformational states; and (b) every non-stationary (externally induced) state terminates with the stationary state.

These two assumptions suffice for the appearance of the following effect: every external action exerted on $E_1 + E_2$, giving rise to a nonstationary state, eventually terminates by the decoherence process selecting a definite conformation for every single molecule in a solution. In general, when compared to the initial conformation-distribution, the final conformation-distribution (of an ensemble of molecules in a solution) exhibits the change of conformation of a certain (non-

negligible) fraction of the molecules in a solution. This is *effectively* the conformational transition taking the time of the order of the "decoherence time" τ_D, which is typically negligible on the macroscopic scale [15]. So, in effect, Levinthal's paradox disappears in the model considered [5,6]. The more specified mechanism of both the nonstationary state as well as of the stationary state (that is described by the decoherence of the conformational states) is an open issue of the model [5,6]. To this end, the work is still in progress.

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