



Hofmeister series: The quantum mechanical viewpoint

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ABSTRACT

It is suggested that electromagnetic quantum vacuum fluctuations are at the very deep root of the so-called “specific ions effects” in concentrated solutions or in living cells. A many-body quantum-mechanical frame of thinking is proposed based on the concept of quantum coherence taking into account explicitly density and excitation frequencies of molecules and/or ionic species. It is also proposed that Hofmeister phenomena could have a natural explanation in the harmonic relationships between sets of characteristic frequencies ruled by quantum mechanical laws. It then follows that physical chemistry of concentrated media and biology should be ruled more by a quantum “symphony” between indistinguishable constituents rather than localized two-body electrical interactions between molecular or ionic species.

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1. Introduction

Quantum mechanics was introduced some 90 years ago to explain the amazing fact that a negatively charged electron approaching a positively charged proton at a distance less than 1 pm experiences an overall repulsive force and not an attractive one, as one would naïvely assume, based on Coulomb's law. The nature of this repulsive force may be traced back to an uncertainty relationship, $\Delta p \cdot \Delta x \geq \hbar/2$, introduced in 1927 by Werner Heisenberg [1], linking the spreading in position Δx to the spreading of momentum Δp through a quantum of action $\hbar \approx 0.65821 \text{ eV} \cdot \text{fs}$. Accordingly, the electron having a mass $m_e = 0.511 \text{ MeV} \cdot c^{-2}$ has both kinetic energy $U_{\text{kin}} = \Delta p^2/2 m_e \approx (\hbar/\Delta x)^2/2 m_e$ and potential energy $U_{\text{pot}} = -\alpha \cdot (\hbar \cdot c)/\Delta x$, where $\alpha \approx 1/137$ is Sommerfeld's fine structure constant and $c = 299,792,458 \text{ m} \cdot \text{s}^{-1}$ is Einstein's constant. Plunging in numbers, it thus transpires that $(U_{\text{kin}}/\text{eV}) = 0,038/(\Delta x/\text{nm})^2$ and $(U_{\text{pot}}/\text{eV}) = 1,44/(\Delta x/\text{nm})$, showing that close to the nucleus ($\Delta x \approx 0,01 \text{ pm}$), repulsion ($U_{\text{kin}} = +380 \text{ MeV}$) dominates over attraction ($U_{\text{pot}} = -1.44 \text{ MeV}$). Sending away the electron at a larger distance ($\Delta x = 0,1 \text{ nm}$) shows that attraction ($U_{\text{pot}} = -14.4 \text{ eV}$) now dominates over repulsion ($U_{\text{kin}} = +3.8 \text{ eV}$). Consequently, electrons will neither be found close to the nucleus, nor be found very far away from it.

The above considerations are fundamental and quite general and shows that quantum mechanics is the right way of thinking as soon as electrostatics fails to explain experimental findings. One may also reformulate the problem in terms of density instead of distance. When the

electron is close to the nucleus, the electronic density is high and quantum effects matters, whereas when the electron is far from the nucleus, the electronic density is low with quantum mechanical effects appearing as small fluctuations around an average value ruled by electrostatics alone.

Reformulating the problem in terms of density then means that quantum mechanics matters as soon as density for solvents or concentration for solute species becomes higher than a characteristic threshold. For water, this density threshold corresponds to the density at the critical point $\rho^* \approx 0.322 \text{ g} \cdot \text{cm}^{-3}$. Accordingly, below this critical density, water will always exist as a gas having properties well described by classical statistical physics. Above this threshold, water forms a liquid with so tightly packed molecules, that a “specific” interaction named “hydrogen bonding” should be invoked in order to explain physical and chemical properties. In fact, one should keep in mind that invoking such a specific interaction between water molecules is a consequence of deliberately ignoring quantum mechanical effects that have to be considered owing to the high-density situation. Being afraid of solving the quantum mechanical problem, one relies on classical physics using *ad hoc* models where water molecules of definite size are engaged into putative hydrogen bonds [2].

The same attitude is adopted as soon as solute concentrations becomes higher than 100 mM, as again, instead of solving the full quantum mechanical problem, one invokes “specific ions effects” in order to stay at a classical level of thinking in terms of ions of definite size disrupting (chaotropes) or reinforcing (kosmotropes) a putative structure in the solvent. In biology, such puzzling “specific ion effects” were discovered about 150 years ago by Franz Hofmeister, leading to the so-called Hofmeister's series [3,4]. The fact that a full theoretical explanation of

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the ordering of these ions is still lacking should be put in mirror with the fact that nobody really knows how to define clearly what is a hydrogen bond [2].

Taking for granted that specific ions effects that cannot be fully explained by electrostatics are to be associated to quantum effects is the starting point of this essay. It is worth noting that by making this crucial step, we do not claim to go on the right track. We are perfectly aware that we could even be completely wrong and that it is perfectly possible that quantum mechanics and specific ions effects in biology cannot be related. Our motivation for thinking quantum lies in the fact that after more than 150 years of classical thinking, Hofmeister phenomena remain a deep mystery. But before invoking quantum effects, one should have a clear mind about what is quantum mechanics. This is particularly crucial for biologists that have not been trained to leave Newtonian real 3D-space in order to land in complex abstract Hilbert's or Fock's spaces. The next section is thus devoted to a non-mathematical presentation of quantum mechanics principles in relation with condensed matter situations such as found in liquids, solutions or in a cell. In another section we will present the main consequences of thinking quantum in the case of water. Finally, in the last section, the problem of ions and nanobubbles will be addressed using these new conceptions about what is really this thing called "water".

2. Quantum mechanics for biologists

Who has not hear or read about Richard Feynman's famous quote about quantum mechanics: « *I think I can safely say that nobody understands quantum mechanics* » [5]? Was this a simple joke from a facetious man, or a deep truth about the way Nature is working? Nobody knows, but there are clues in scientific literature that it was indeed a joke. A first clue is given by a series of very interesting papers published in the forties by a couple a French mathematicians [6–9]. The main conclusion that could be drawn from these papers is that quantum mechanics could be defined in one single sentence made of very few words: « *There is no state variable* ». All quantum formalism can be deduced from this simple principle.

In order to understand how quantum rules emerge from this simple sentence, one must first consider that if all physical quantities are in theory simultaneously measurable, then a state variable should exist. What is called a state variable is a variable from which all others variables may be derived. This is the standpoint of classical mechanics. In turn, if there are quantities that are not simultaneously measurable, there can be no state variable. This is the standpoint of quantum mechanics. The absence of state variable gives an essential uncertainty and means that there exist by right two quantities that are not simultaneously measurable.

Such uncertainty implies that some predictions are prone to fundamental errors and should thus be expressed in terms of probabilities. Thus, considering for a physical quantity A the whole set of certain predictions (X_1, X_2, \dots, X_n) one should by principle express any prediction X as a linear combination $X = c_1 \cdot X_1 + c_2 \cdot X_2 + \dots + c_n \cdot X_n$ (spectral decomposition principle). Then, the probability of observing the element X_i is an arbitrary function $f(c_i)$ of the associated coefficient c_i . If one further requires that the unknown function f should be the same for any spectral decomposition, it is possible to show that it should be such that $f(x \cdot y) = f(x) \cdot f(y)$, where x and y are complex numbers, that is to say numbers having both a magnitude r and a phase φ : $z = r \cdot \exp(i \cdot \varphi)$. The further requirement that f is a continuous function then leads to the only acceptable solution: $f(x) = |x|^k$, with $k > 0$ [6]. Finally, using a generalized version of Pythagoras' theorem, it was possible to show that only two values of k are possible: $k = 1$ (existence of a state variable, Boolean logic) and $k = 2$ (no state variable, non-Boolean logic) [8]. For this last case, the probability of observing a given element is thus given by the square of the corresponding complex coefficient in the linear superposition, one of the base postulates of quantum theory [10].

The next step is to introduce the basic two quantities that cannot be simultaneously measured. As we are seeking a quantum theory for high-density systems the number of available quanta N emerges as a crucial variable. Allowing some fluctuations ΔN in the number of quanta, it may be shown that the conjugate variable is necessarily the quantum phase φ with a fundamental uncertainty relationship [11]:

$$\Delta N \cdot \Delta \varphi \geq \frac{1}{2} \quad (1)$$

The crucial point here is that only pure numbers having no units are involved. This means that such an uncertainty relationship is scale invariant, that is to say, that quantum mechanics is the right way of thinking at any scale, atomic or macroscopic. The implication is that there is no fundamental distinction between observer and observed system, between quantum and classical system. Here, the classical way of thinking is obtained when the total number of quanta can be determined with certainty, i.e. when $\Delta N = 0$. The consequence is that the phase φ is then a random variable that changes in a completely arbitrary way from one quantum to another one (incoherence). But, if the total number of quanta is not known with certainty, then the quantum phase may take a well-defined value ($\Delta \varphi \rightarrow 0$) when $\Delta N \rightarrow +\infty$. This situation describes a quantum regime that is routinely observed at a macroscopic scale in ferromagnetism, ferroelectricity, superconduction and superfluidity phenomena for instance. Quantum means here appearance of a collective many-body coherent behavior that cannot be explained by considering only pairs of interacting quanta.

It is this kind of quantum coherence typical of high-density situations that is pertinent in liquid water [11] and of course in biology [12]. Most importantly, it cannot be observed in diluted cases ($\Delta N \rightarrow 0$). The quite interesting point is that a "quantum" is not necessarily an elementary particle, but it can be an ion, a molecule, a protein, cell or even a bird or a fish. That is to say a quantum is anything that can be considered at a given scale as a whole unit, not separable into smaller parts. To make the argument clear, let's talk about birds, considering not a single bird but a swarm of birds. Have you noticed that when it is possible to count exactly the number of birds in the swarm (dilute case), then the movement of each bird appears as erratic and unpredictable? But, above a certain number of birds per unit volume, it becomes impossible to count them individually ($\Delta N > 0$) and as a consequence, a collective behavior emerges above a certain critical threshold. The whole swarm is now moving with a wonderful collective and coherent smooth behavior instead of being erratic and random. The same applies of course in shoals of fishes.

These examples show that the scale invariance of relation (1) associated to the existence of creation and annihilation operators in quantum field theories [11] is a tangible reality at all scales, provided that one faces a high density situation. In fact, it can be shown that any coherent quantum system would display as a whole a classical behavior, with a predictable trajectory computable according to the least action principle [13]. In other words, classical mechanics is just a high-density approximation of quantum mechanics when phase coherence emerges.

But we also know from thermodynamics that any macro-state M whether in equilibrium or not, has a non mechanical entropy $S(M) = k_B \cdot \log W(M)$, where $W(M)$ is the phase space (position, momenta) volume compatible with a set macro-variables allowing to define precisely the macro-state. As shown by Edwin Thompson Jaynes, the second law stating that $S(\text{initial}) \leq S(\text{final})$ directly follows from Liouville's theorem, expressing the necessary condition for a change from a macro-state M_i to another macro-state M_f be reproducible by any observer able to control only the set of macro-variables defining the macro-state M [14].

In order to set a quantitative link between entropy and quantum mechanics, let's consider a set of N particles of mass m enclosed in a cube of edge L in thermal contact with a thermal bath fixing the number of microstates (positions q and associated momenta p) that are accessible to this ensemble. Owing to Brownian motion, any particle has equal probability to be found at any location in the volume $V = L^3$ leading to

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