QUANTUM COHERENT WATER

From dr Mae- Wan-Ho

Water, the simplest, commonest compound on earth, also has the most complex properties and baffling ‘anomalies’ that make it essential for life. Generations of brilliant scientists have pitched their wits and sophisticated instrumentations in the hope of unravelling the secrets of water but in vain.

Perhaps the most significant discovery within the past 30 years is that water has quantum properties under ambient conditions, and may even be quantum coherent, as revealed by nuclear magnetic resonance measurements (see Cooperative and Coherent Water and other articles in the series, *SiS* 48).

However, neither classical nor standard quantum theory predicts quantum coherence for water, largely because they ignore quantum fluctuations and the interaction between matter and electromagnetic field, which are taken into account in a quantum electrodynamics (QED) field theory.

Quantum fluctuations and coupling between matter and electromagnetic field in QED indeed predicts quantum coherence for liquid water even under ordinary temperatures and pressures, according to Emilio Del Giudice and his colleagues at Milan University, who have been researching this problem since the 1990s. Their theory suggests that interaction between the vacuum electromagnetic field and liquid water induces the formation of large, stable coherent domains (CDs) of about 100 nm in diameter at ambient conditions, and these CDs may be responsible for all the special properties of water including life itself.

Quantum electrodynamics of condensed matter and water.

Quantum field theory explicitly recognizes an extended vacuum field – ‘zero point field’ – interacting with matter, as well as quantum fluctuations whereby energy in the vacuum field in the form of photons could be captured by matter. Quantum field theory combines Heisenberg’s uncertainty principle in quantum mechanics with the energy-matter equivalence of Einstein’s special relativity [6]; in other words, $DE \sim 1/Dt$ is combined with $E = mc^2$.

Quantum field theory began in the 1920s and 1930s with the work of Max Born, Werner Heisenberg, Paul Dirac and others, and later, Richard Feynman and Freeman Dyson. But standard quantum field theory still does not explain water adequately.

In standard quantum field theory, the energy levels of material systems are shifted by their interaction with the fluctuations of the electromagnetic (EM) fields in the vacuum. The first clear example was the “Lamb shift”, the energy of an electron surrounding the proton in a hydrogen atom is slightly lower than the value calculated from the atomic theory based on purely static forces. Although this shift is very small, it provided evidence of the quantum vacuum fluctuation that has to be understood within the framework of quantum electrodynamics. In the case of the hydrogen atom, the effect is due to the interactions between the electric current of the electron orbiting the nucleus and the fluctuating electromagnetic field of the surrounding space (vacuum).

For a collection of particles, the usual approach is to apply the Lamb shift to each particle separately. While this is correct for very low density systems like gases, where the distance between any two particles is larger than the wavelength of the relevant fluctuating fields coupled to the systems, dense systems – condensed matter or liquids and solids - show entirely different behaviour.

When energy is absorbed from the vacuum field, the particles will begin to oscillate between two configurations. In particular, all particles coupled to the same wave-length of the fluctuations will oscillate in phase with the EM field, that is, they will be coherent with the EM field. The total energy of the system, E_{tot}, is a combination of the energy of the fluctuating EM field, E_{fl}, and the energy of excitation of the particles shifted from their ground state to the excited configuration, E_{exc}, plus the E_{int} of the Lamb-like shift,

$E_{\mathrm{tot}} = E_{\mathrm{fl}} + E_{\mathrm{exc}} + E_{\mathrm{int}}$

While E_{fl} and E_{exc} are positive, E_{int} is negative. As shown by Preparata in 1995 E_{fl} and E_{exc} are proportional to the number N of particles in a coherence domain (CD), but E_{int} is proportional to $N\sqrt{N}$. Consequently, there is a critical number of particles N_{crit} enclosed in a CD for which $E_{\mathrm{tot}} = 0$. At that point, a phase transition occurs. The coherent oscillations of the particles in the CD no longer require any external supply of energy, and the oscillation is stabilized. Moreover, the CDs will begin to attract more molecules, and attract each other, thereby turning gas into liquid in a change of phase. With further increase in density, the system becomes a net exporter of energy because the stabilized coherent state has a *lower* energy than the incoherent ground state (see later).

The size of the CD is just the wavelength l of the trapped EMF. The collective coherent oscillation of the molecules in the CD occurs between the coherent ground state and an excited state, whose volume, according to atomic physics, is wider than the ground state volume. The wavelength l of the trapped EMF, and hence the size of the CD is about 100 nm, as it depends on the excitation energy E according to the equation:

$l = hc/E_{exc}$

The CD is a self-produced cavity for the EMF; the photon of the trapped EMF acquires an imaginary mass, and is therefore unable to leave the CD. Because of this self-trapping of the EMF, the frequency of the CD EMF becomes much smaller than the frequency of the free field having the same wavelength. This result applies to all gas-liquid transitions.

Coherent water is a source of almost free electrons.

The special thing about water is that the coherent oscillation occurs between the ground state and an excited state at 12.06 eV (electron volt), which is just below the ionizing threshold at 12.60 eV, when $H_2O \rightarrow 2H^+ + O^{2-}$. A liquid water CD of 100 nm diameter contains millions of water molecules, and includes an ensemble (or plasma) of millions of almost free electrons that can be donated readily to electron acceptors dissolved in the water.

Some 60 years ago, the father of biochemistry, Hungarian born US scientist Albert Szent-Gyorgyi had already highlighted the importance of water for life [8, 9], and proposed that organized water existing close to surfaces such as cell membranes, is able to induce a very long lasting electronic excitation of the different molecular species present, thereby activating them and enabling their mutual attraction for reactions to take place (see later).

According to calculations performed by Preparata, Del Giudice and colleagues, the water CD is a quantum superposition of ground coherent state and excited state in the proportion of 0.87 and 0.13, giving an average energy of excitation per molecule of 1.56 eV. This is combined with the energy of the fluctuation electromagnetic field of 3.52eV and the interaction energy of -5.34 eV, according to equation (1), thus resulting in a *negative* energy of -26 eV per molecule. The renormalized (physically observable) frequency of the trapped EMF in the CD corresponding to 0.26 eV is 6.24 x 10^{13} Hz in the infrared region.

Liquid water is therefore a two-fluid system (in analogy with superfluid helium) consisting of a coherent phase (about 40 percent of total volume at room temperature) and an incoherent phase. In the coherent phase, the water molecules oscillate between two electronic configurations in phase with a resonating EMF. The common frequency of the EMF and the electronic oscillation of the coherent phase being 0.26 eV; whereas the energy difference of the two electronic configuration of the coherent phase is 12.06 eV, which gives the wavelength of 1 000 A (100 nm) of the coherence domain. The remaining 60 percent incoherent phase is extracted by thermal fluctuations from the coherent phase. The two phases have widely different dielectric constants: that of the coherent phase is 160, due to the high polarizability of the coherently aligned water molecules that are oscillating in concert; while the dielectric constant of the incoherent state is about 15. The externally applied electric fields are therefore only felt in the non-coherent phase.

This picture of liquid water, according to Del Giudice and colleagues, is reflected in the many observations supporting a two-state model of water (see Two-States Water Explains All? *SiS* 32), in which a substantial fraction of the molecules exist in hydrogen bonded state resembling that of ordinary ice. In fact, the hydrogen-bonds - short range interactions – are the consequence of the induced coherence in the coherence domains. But there is a rapid interchange of molecules between the CDs and the incoherent phase, hence it is impossible to detect CDs when the detection time is longer than the period of the oscillations, which is less than 10^{-13} s.

Quantum coherent water and life

Oxidation and reduction or redox reactions are the stuff of energy transduction in living organisms. It involves transfer of electrons from one substance (donor) to another (acceptor) to power all living activities. But where does the electron come from? It comes ultimately from splitting water in photosynthesis by green plants and cyanobacteria. However, it takes 12.60 eV to split water, an energy corresponding to soft X-rays, which is not what the green plants and cyanobacteria use.

More than 50 years ago, Szent-Gyorgyi [9] suggested that water at interfaces was the key. He proposed that water in living organisms existed in two states: the ground state and the excited state, and that water at interfaces such as membranes existed in the excited state, which requires considerably lower energy to split. A sign of the excited water is that a voltage should appear at the boundary between interfacial water and bulk water, which was indeed observed. This property of water enables energy transfer to take place in living organisms ensuring long-lasting electronic excitations. Szent-Gyorgyi's ideas were largely ignored by the scientific mainstream that became obsessed instead with molecular genetics.

The anomalous water at interfaces has been the subject of numerous research papers and reviews, and was already known in the late 1940s, as Del Giudice and colleagues point out. Most if not all water in living organisms is interfacial water, as it is almost never further away from surfaces such as membranes or macromolecules than a fraction of a micron.

A vivid demonstration of interfacial water was achieved by Gerald Pollack's research team at University of Washington, USA (see Water Forms Massive Exclusion Zones, *SiS* 23). Using a hydrophilic gel and a suspension of microspheres just visible to the eye, they showed that interfacial water apparently tens of microns or even hundreds of microns thick forms on the surface of the gel, which excludes the microspheres as well as other solutes such as proteins and dyes, and hence referred to as an 'exclusion zone' (EZ). Formation of EZ depends on fixed charges on the gel. When negatively charged gels were used, a potential difference of -150 mV was measured, in line with Szent-Gyorgyi's prediction, and protons were also excluded, becoming concentrated just outside the exclusion zone, giving a low pH there. Many other unusual characteristics were found [13]. EZ water is about 10 times as viscous as bulk water, it has a peak of light absorption at 270 nm, and emits fluorescence when excited by light at this wavelength. Illumination of EZ water especially by infrared increases the depth of the layer.

Del Giudice and colleagues [4] suggest that EZ water is in fact a giant coherence domain stabilized on the surface of the attractive gel. Inside the cell, the EZ would form on surfaces of membranes and macromolecules, as envisaged by Szent-Gyorgi. Because coherent water is excited water with a plasma of almost free electrons, it can easily transfer electrons to molecules on its surface. The interface between fully coherent interfacial water and normal bulk water becomes a "redox pile". In line with this proposal, EZ water does indeed act as a battery, as Pollack's research team demonstrated (see Liquid Crystalline Water at the Interface, *SiS* 39).

Del Giudice and colleagues also argue that water CDs can be easily excited, and are able to collect small external excitations to produce single coherent vortices whose energy is the sum of all the small excitation energies, turning the originally high entropy energy into low entropy coherent energy, which is trapped stably in the water CDs. This coherent energy in turn enables selective coherent energy transfer to take place as follows. All molecules have their own spectrum of vibrational frequencies. If the molecule's spectrum contain a frequency matching that of the water CD, it would get attracted to the CD, and become a guest participant in the CD's coherent oscillation, and settle on the CD's surface. Furthermore, the CD's excitation energy would become available to the guest molecules as activation energy for chemical reactions to take place. This selectivity may be the reason why out of a hundred different amino acids only 20 have been selected for making proteins in living organisms.

There is indeed independent evidence that molecules taking part in a biochemical reaction do share a common frequency, which is how they attract each other, essentially by resonating to the same frequency (see [15] The Real Bioinformatics Revolution, *SiS* 33). So it is likely that the reactants are attracted to the surface of the same water CDs, where the reaction will takes place, greatly facilitated by the excitation energy of the water CD. After the reaction, the energy released can also be absorbed by the water CD, shifting the CD's oscillation frequency, and hence changing the molecular species that become attracted to it, thereby in principle, facilitating the next reaction to take place in a chemical pathway.

Quantum coherence of water is really what makes life possible. It could also account for other strange phenomena such as the formation of a 'stiff' water bridge floating in the space just above two beakers of water placed next to each other and subjected to a strong electric field, as explained by Del Giudice and colleagues elsewhere [16], as well as low energy nuclear reactions (or cold fusion) [17], non-thermal electromagnetic field effects on biological system and possibly homeopathy

Cooperative and Coherent Water

Cooperative hydrogen-bonding between molecules gives rise to energetically favourable three-dimensional network of supramolecular clusters in liquid water under ambient conditions, resulting in long-range dipole correlation and quantum coherence.

As a self-confessed hydrophiliac, I love nothing more than to immerse myself in water, literally and figuratively. I have been obsessed with water's unfolding biopic as though my own life depends on it.

Water is the simplest, commonest chemical compound on earth. Yet, it has the most complex properties and baffling 'anomalies' compared to its neighbours in the periodic table of chemical compounds, without which life as we know it would be impossible. Water has remained a mystery to generations of the best scientists who have pitched their wits (and sophisticated instruments) at water, only to have it slip gracefully through their fingers.

Water is perfectly transparent and has no colour, except when its fine droplets refract sunlight into the dazzling spectrum of the rainbow. Water has no form other than that of the containing vessel, no sound, no movement, and little resistance; except when coaxed by the gentle breeze into smiling ripples, or tickled into undulating waves lapping like laughter. Or else when whipped up by hurricanes into howling surges that hurl ships into the air, or heaved by submarine earthquakes into rumbling tsunamis that deluge shore and land.

The dramatically different, infinitely varied moods of water are the stuff of life itself, if not also great art. Indeed, a good scientific theory needs to capture the art, to explain the long range cohesion coalescing massive volumes into gigantic whirlpools, and at the same time bespeaks the endless diversity in molecular structures that makes every snowflake a unique event in the history of the universe.

This latest episode brings together evidence, old and new, that confirms what many of us had suspected: water is coherent, if not quantum coherent, and it is that which accounts for all its life-giving properties. We begin with some basics on which almost everyone agrees.

Water loves bonding.

The water molecule with separated positive and negative charges

The water molecule is a permanent dipole in which positive and negative charges are separated, with the two hydrogen atoms at the positive pole and the oxygen atom at the negative pole. Like other dipoles, water molecules can stack together in dipole interactions with alternating positive and negative poles next to each other. It can also engage in electrostatic interactions with charged ions and other dipoles dissolved in it.

In addition, the water molecule likes to hydrogen-bond with one another (Fig. 2), and with molecules and ions dissolved in it. A hydrogen bond consists of hydrogen shared between two electronegative atoms such as oxygen or nitrogen. The compound or group that donates the hydrogen is the hydrogen donor, while and compound or group that accepts the hydrogen is the hydrogen acceptor. Water is both hydrogen donor and acceptor; it can donate two hydrogens and its oxygen can accept two other hydrogens. The water molecule is generally represented as a tetrahedron with four ‘arms’ – two hydrogen donors and two hydrogen acceptors - pointing at the vertices. This tetrahedral structure is typical of ordinary ice, where all the water molecules are cross-linked in a crystalline, hexagonal array.

Hydrogen-bonded water molecules

Decades of research has resulted in a near-consensus that water at ambient temperatures and pressures exists as a dynamic network of supramolecular clusters where a proportion of the molecules are linked together by ‘flickering’ hydrogen bonds, similar to those in ordinary ice. It is also widely acknowledged that the hydrogen-bonded network of liquid water accounts for most, if not all its anomalous properties. Beyond that, there is no agreement over the exact proportion of molecules linked by tetrahedral ice-like bonds, the precise structure and size of the clusters, how freely the molecules can move around, and especially whether interactions are strictly local with nearest neighbour, or much more global in extent.

Within the past decade, substantial evidence has emerged indicating that cooperative interactions between molecules results in remarkably long-range coherence in liquid water under ambient conditions.

First of all, water has an unusually high dielectric constant of ~78 at room temperature, making it the most important polar solvent in chemistry and biology, it also means it is easily polarised by an electric field. The dielectric constant, or relative static permittivity, is a measure of the extent to which it concentrates electrostatic lines of flux relative to a vacuum. Researchers led by Manu Sharma at Princeton University, New Jersey, USA, have shown by molecular dynamics simulations from first principles that the high dielectric constant of water is due to two effects of the hydrogen bonds contributing in almost equal measure. The hydrogen bonding serves to align the dipoles and at the same time, pull away positive and negative charges within a molecule, enhancing the average molecular moment.

Cooperativity through hydrogen bonds.

Cooperativity in chemistry is the tendency of individual chemical interactions to influence each other, so that local actions can have global effects, and *vice versa*; the whole being greater than and not predictable from the sum of the parts. That's how organism work, and why water is so vital for life (see Quantum Jazz Biology).

Quantum chemist Roger A. Klein at Bonn University in Germany has demonstrated from electronic and quantum chemical computations that cooperativity is involved in the formation of hydrogen-bonded supramolecular clusters.

Different forms of ice are all variations on the theme of tetrahedral molecules arranged in the form of hexagons, or six-member rings, as determined by X-ray and neutron diffraction. It is therefore reasonable to think of liquid water as flickering clusters of interlocking hexagonal rings, with some long range order extending on average to at least the second or third nearest neighbour; which is compatible with data from X-ray or neutron scattering experiments.

In gas clathrates – where gases such as methane are caged in ice at the bottom of the Arctic Ocean – the water molecules tend to form pentagonal arrays of cages fused along the edges.

Cooperativity is involved in the formation of the six- and five-member rings, as evident in the greater stabilizing energy and higher electron density at 'bond critical point' (bond strength) for each hydrogen bond in the cluster compared to a single hydrogen bond between two water molecules (dimmers). The higher electron density and bond strength is a consequence of the shortening of the hydrogen bonds within the cluster compared with that in a dimmer.

Cooperativity shortens (left) and strengthens the hydrogen bonds.

Increasing cooperativity is more associated with a greater proportion of tetrahedral ice-like bonds in water clusters than with cluster size alone, once an optimal ring size of five or six water molecules has been reached. Thus, it is no accident that the hexagonal motif is common in liquid water and ice, and the edge-fused pentagonal motif in gas clathrates. Both are optimised for cooperative interactions, which in turn make it likely for large clusters to form. There is evidence that large clusters actually exist in liquid water under ordinary conditions, making coherent energy transfer possible.

Resonant energy transfer through hydrogen-bonded network.

At a temperature of 300 K (≡ 27 ˚C), ~90 percent of water molecules are hydrogen-bonded, a picture supported by molecular dynamics simulations and a large body of experimental evidence. The structure of the hydrogen bond network fluctuates on time scales ranging between 10 fs (femtosecond, 10^{-15} s) and ~10 ps (picosecond, 10^{-12} s), and includes changes of molecular orientations and distances, hydrogen bonds breaking and reforming, and slower rotational motions.

The O-H bond stretch vibration exhibits a 270 cm^{-1} wide band (in wave number, an alternative way of expressing frequency) centred at ~3 400 cm^{-1} in the infrared region. As temperature decreases, the maximum of the band shifts to lower frequencies and the envelop changes shape, indicating an overall enhancement of hydrogen bonding. The O-H bond stretching vibration is a sensitive indicator of structural and dynamical fluctuations in the extended hydrogen-bonded network.

Two-dimensional infrared photon echo (2DIR-PE) spectroscopy has been added recently to the armoury of techniques for probing water. The technique depends on exciting (pumping) the O-H bond stretching vibration with infrared light, and looking for the response (echoes) in the infrared spectrum.

Using 2DIR-PE spectroscopy, researchers at the University of Toronto, Canada, and Max-Born Institute for Nonlinear Optics in Berlin, Germany, discovered ultrafast resonant transfer of excitation energy between water molecules that takes place via dipole coupling in the hydrogen-bonded network [6]. The energy transfer time of ~80 fs is unaffected by temperature from 340 to 274 K [7]. This transfer time in pure water is substantially faster than the 700 fs previously measured in a D_2O:H_2O mixture, where resonant energy transfer is obstructed, and is also much shorter than the average hydrogen bond lifetime of ~1ps.

The experiment carried out at different temperatures showed that frequency correlations (between excitation and echo) due to local structures are lost in about 50 fs at high temperatures (hinting at a much more flexible hydrogen-bonded network). But at lower temperatures these correlations are longer-lived. At 274 K (just above freezing), a dramatic change takes place, and the frequency correlations persist beyond ~200 fs, indicating that the hydrogen-bonded supramolecular structures are stabilized.

Large supramolecular structures in water.

Liquid water at ambient temperatures is traditionally regarded as a homogeneous phase, with the same average structure everywhere. However, some scientists, beginning with Wilhelm Conrad Rőntgen who won the 1901 Nobel Prize for the discovery of x-rays, believe that the anomalies of water are best explained if liquid water is an equilibrium mixture of two states that differ in density.

Recently, researchers at Stanford University in California, USA, provided fresh evidence that liquid water is indeed inhomogeneous over a length scale of about 1 nm [8]. Combining small angle x-ray scattering, which gives information on the size of supramoleular structures, with x-ray emission and x-ray raman scattering, which yield information on hydrogen bonding, the researchers were able to show that water at ordinary temperatures exists in two distinct states (with no intermediates): low density water (LDW) in which the molecules are hydrogen-bonded in ice-like tetrahedral bonds; and high density water (HDW) in which the molecules are linked by more distorted hydrogen-bonds. Hence, density fluctuations occur over the length scale of ~1.2 nm. The length scale of ~1.2 nm encompasses about 70 molecules of water. It is tempting to equate that with the inner core of Martin Chaplin’s icosahedron containing 280 molecules of water, which he has proposed as the predominant supraomolecular structure of water under ambient conditions. The icoshedron is composed of 20 identical units of 14 hydrogen-bonded molecules, five of which are in the inner core.

At 24 ˚C, the proportion of light water with ice-like tetrahedral bonds is about 28.6 percent, and only disappears completely at boiling point.

Quantum effects in water.

More and more researchers are coming around to the view that quantum effects need to be taken into account in molecular dynamic simulations of water in order to reproduce and interpret a range of experimental results [9]. Kim Hyeon-Deuk and Koji Ando at Kyoto University, Japan, believe that quantum effects play a key role in the dynamics of the hydrogen-bonded network, and are therefore essential for understanding the anomalous properties of water.

Nuclear quantum effects – effects due to the nuclei of atoms - have a significant impact on the behaviour of water. This is evident in the large changes observed in numerous properties of water when hydrogen (H) is substituted by its heavier isotopes deuterium (D) and tritium (T). For example, the melting of D_2O is 3.82 K higher than that of ordinary water, and the effect is even more pronounced in T_2O.

Evidence for nuclear quantum effects in water is steadily growing. Recently, researchers at several institutes in Madrid, Spain, demonstrated that nuclear quantum effects have to be included in molecular dynamic simulations in order to reproduce experimental heat capacity measurements over a wide range of temperatures encompassing ice and liquid water. They regard the heat capacity of water “a signature of nuclear quantum effects” .

Francesco Paesani and colleagues at the University of California La Jolla, USA, investigated the molecular reorientation associated with the dynamics of the hydrogen-bonded network in liquid water using quantum molecular dynamic simulations. They found the calculations in excellent agreement with the corresponding experimental results obtained at different temperatures with polarization resolved, femtosecond infrared, spectroscopic measurements. Comparison with the results obtained using classical molecular dynamics simulations clearly indicated that the explicit inclusion of nuclear quantum effects is critical for reproducing the experimental results.

Evidence of quantum coherence from nuclear magnetic resonance experiments

Water not only possesses quantum properties; it may actually be or become quantum coherent. Evidence for quantum coherence in water has come from unexpected observations in nuclear magnetic resonance experiments (see Box) over the past twenty years. These are intermolecular multiple quantum coherence signals generated by the collective effects of the dipole coupling of the spin of each molecule with that of every other in the sample, up to 1 millimetre apart. This implies that all the spins of the molecules in the sample are correlated, and driven by the same (electromagnetic) field to oscillate *in phase*.