

Two-dimensional Proton Conductors

William S. Page
Daneliuk & Page

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1 Introduction

An enormous literature has developed on the subject of the abnormal mobility of protons in aqueous solutions. Eigen and De Maeyer in 1958 [1] may have been among the first to observe that "The proton transport in hydrogen-bonded media is completely different from normal ionic migration and corresponds more to electronic transport processes in semi-conductors. ... Phenomenologically, the ice crystal may be considered as a 'protonic semi-conductor' with an intrinsic (thermal) distribution of the charge carriers (protons) between a 'valence' band (H-bonded H_2O) and a 'conduction' band (excess protons fluctuating in H-bonds). As an elementary particle the proton has much more in common with the electron than any other ion, the radii of which are of completely different order of magnitude.". Eigen and De Maeyer describe a "protonic rectifier" based on "The combination of two crystals, one doped with a proton donor (HF , F^- being almost immobile) and the other one with an acceptor ($LiOH$, NH_3 , Li^+ or NH_4^+ being immobile)...".

The bond structure of ice (and to a large extent liquid water as well) involves two protons (hydrogen atoms) per oxygen atom in a 3-dimensional, approximately tetrahedral structure, i.e. the oxygen atoms occupy the corners of a tetrahedron while the hydrogen atoms form the bonds between pairs of oxygen atoms along the edges of the tetrahedron. While each oxygen atom is surrounded by four hydrogen atoms, each primitive cell of the lattice is occupied by an H_2O molecule as expected. Similar to the electrons in conventional semiconductors, in pure water almost all of the hydrogen is in the "valence" band state. Each oxygen atom has two loosely bound hydrogen atoms which form hybrid hydrogen "orbitals" with four tetrahedrally coordinated neighboring oxygen atoms. Defects in this structure are classified as L-defects (empty hydrogen bonds, expressed in molecular terms as the hydroxyl ion OH^-) and D-defects (doubly occupied hydrogen bonds, expressed in molecular terms as the hydronium ion H_3O^+). An L-defect can also be described as a "proton hole" in the valence band, while a D-defect corresponds to a proton in a conduction band.

Thermal disruptions of the lattice structure give rise to a small number of defects in this structure. In some cases two hydrogen atoms may occupy a single hydrogen-bond creating a D-type defect. In pure water, each D-type defect is accompanied by a corresponding L-type defect. It is the movement of these defects which give rise to the protonic conductivity of water.

In the case of substitutional impurities such as ammonia NH_3 the N atom is an H-donor. The extra H atom does not fit into the regular hydrogen bond structure and there is therefore an excess of D-type defects. The result is that these extra protons are relatively free to hop from one already occupied hydrogen bond to the next. In the case of substitutional impurities such as hydrogen fluoride HF the F atom is an H-acceptor - introducing "holes" in the structure. One of its structurally-expected hydrogen bonds is empty and there is therefore an excess of L-type defects over pure water. It is now the absence of a proton in a hydrogen bond that moves throughout the lattice.

Water with an excess of D-defects is called a D-type electrolyte (analogous to N-type electron semiconductor). Water with an excess of L-defects is called an L-type electrolyte (analogous to P-type electron semiconductor). Both L-type and D-type electrolytes are good proton conductors. L/D-type junctions produce proton current diodes with properties similar to their electron counterparts. In particular such diodes display rectification (unidirectional current flow), high values of thermoelectric power, and may display luminescence under forward bias due to recombination of L and D-defects. Such effects as thermoluminescence of ice following irradiation [10] and sonoluminescence of water [9] may be related to L/D recombination.

These structural considerations when applied to ice seem straight forward [5]. It also turns out, however, that liquid water to a very large extent retains this tetrahedrally coordinated structure locally. In fact, both ice and liquid water depart from this ideal 3-dimensional structure in fairly subtle and random ways that give rise to the beautiful fractal patterns of snow flakes and frost. It may well be appropriate to treat water as a substance with a "fractal" fractional dimension with liquid water having a dimension between 1 and 2 and ice having a dimension between 2 and 3. In the simplified calculations in this paper we will, however, use only 1-dimensional models.

2 Band States

The detailed structure of the periodic potential that the hydrogen nuclei encounter is the result of the overlap of electron orbitals and Coulomb interactions. Due to the electronic structure of the oxygen atoms, the electrons are all very tightly bound to the oxygen centers. In comparison to the protons, the electrons are not free to move and do not appreciably take part in electrical conduction. Because both the oxygen and hydrogen nuclei are so much more massive than the electrons we can neglect the motion of the electrons and approximate the interaction between hydrogen and oxygen simply in terms of the generalized Morse potential [7]. Analogous to the treatment of electrons in conventional solid state physics, we can describe the quantum motion of hydrogen in many solids and liquids as solutions of the many-body wave equation which take the form of energy bands. In any situation in which a particle moves in a periodic potential, the energy states of that particle are constrained to occur in "bands", i.e. groups of closely spaced discrete energy levels separated by "gaps" or forbidden energies. Each band contains the same number of states - equal to the total number of unit cells in the "lattice", i.e. the number of potential wells in the periodic structure. The gaps between bands arise from Bragg scattering conditions applied to the De Broglie waves of the particles. This has significant implications for the mechanical, thermal and electrical properties of hydrogen-bonded materials.

The lowest energy band is called the valence band. It is the valence band that is responsible for the structural stability of the material. Since protons are spin 1/2 particles, Fermi's exclusion principle allows two such particles (in opposite spin states) to occupy each energy level. In the case of water each unit cell (molecule) contributes two protons to the valence band. Therefore, as in the theory of electronic semi-conductors, we can see qualitatively that at absolute zero temperature water should be a proton insulator. All the potentially mobile protons would be in the valence band and this band would be full - a moderate potential difference is not able to change the energy level of (that is, to accelerate) these protons. At 0° K, the higher energy bands (the conduction bands) are all empty. As the temperature is increased, a small number of the protons from the valence band can be excited across the energy gap into the conduction bands.

As a first step in looking at the structure of water from the point of view a protonic semi-conductor we will estimate the magnitude of the energy gaps between the first few energy bands.

3 Morse Potential

Ignoring the detailed motions of the electrons, as in the theory of diatomic molecules, we can approximate the interaction between an excess hydrogen atom and a structural water molecule in the lattice in terms of the Morse potential [3]:

$$U_r(r) = -D_0 + D_0(1 - e^{-a(|r|-r_e)})^2$$

where D_0 is the energy required to completely dissociate the $H_2O - p$ bond, a is the asymmetry parameter and r_e is the equilibrium value of r_p , the distance between the p and the centre of mass of the H_2O in H_3O^+ .

We will consider the movement of a proton along a linear chain of water molecules. Taking account of the overlapping potential from the five nearest neighbors of each water molecule, the approximate potential energy barrier along the chain can be written as

$$F(x) = \sum_{k=-5}^5 U_r(x + k d_{OO})$$

where d_{OO} is the mean Oxygen-to-Oxygen distance along the chain.

Bockris and Reddy[3] give the value of D_0 as the total hydration energy of a proton or about 266 kcal/mole or 11.543eV. From spectroscopy studies, r_e for water (liquid) is estimated as 0.98 Angstroms and the oxygen to oxygen spacing is approximately $d_{OO} = 2.92$ Angstroms. By an iterative numeric procedure we can determine the value of the asymmetry parameter $a = 1.29455$, such that we obtain the approximate observed value of the cohesive energy of water.

It can be shown using these parameters that there is a significant departure of the potential $F(x)$ from the commonly employed harmonic oscillator potential. It is this difference which gives rise to the particular distribution of the hydrogen band gaps in water discussed below.

4 Band Gaps

In the "almost free" approximation, the size of the energy gap between the proton valence and proton conduction bands is given by degenerate perturbation theory as twice the value of the corresponding Fourier coefficient of the lattice potential (Burns, p257 [2]). The coefficients of the discrete Fourier transform of the lattice potential are given by

$$T(n) = \frac{\int_{-d_{OO}/2}^{d_{OO}/2} F(r) e^{-2 \frac{i\pi n r}{d_{OO}}} dr}{d_{OO}}$$

for $n = 0, 1, 2, \dots$

$$T = [-4.8185, 11.297, 6.6585, 3.6722, 2.2436, 1.4942, 1.0607, .7898, .61, .48492, .39449]$$

(The first band corresponds to $n = 1$).

Gosar and Pintar [6] estimate that the width of the energy bands as 2.2×10^{-3} eV which is much narrower than the band gaps. Note, however, that due to the asymmetry of the lattice potential, the width of the band gaps drops quickly as the energy level increases.

It is interesting to compare the spectrum of light emitted during sonoluminescence with the width of the proton band gaps. One speculative theory on the origin of sonoluminescence is that the alternating compression and de-compression cycles induced by the sound waves excite protons into the upper proton conduction bands. These protons lose energy and relax back to the valence band in quanta determined largely by the size of the band gaps. If this is the case, a cut-off in the luminescence spectrum will be found in the ultraviolet region at approximately 22.6 eV, that being the size of the lowest and largest band gap.

5 Two-Dimensional Proton Conductors

Stern and Howard [8] describe n-channel Metal-Oxide-Semiconductor Field Effect Transistors (n-MOSFET) in the following terms:

An n-type inversion layer is produced at the surface of a p-type semiconductor when the energy bands near the surface are bent down enough that the bottom of the conduction band lies near or below the Fermi level. This band bending can be introduced by applying an electric field to the surface, in a configuration like that shown in FIG 1, ...

The electric field associated with an inversion layer is strong enough to produce a potential well whose width in the z direction, the direction perpendicular to the surface, is small compared to the wavelengths of the carriers. Thus the energy levels of the electrons are grouped in what we call electric sub-bands, each which corresponds to a quantized level for motion in the z direction, with a continuum for motion in the plane parallel to the surface.

One of the aspects that makes this configuration interesting and useful as a amplifying device is that the density of charge carriers in the inversion layer can be controlled by the intensity of the electric field. The carrier density, in turn affects how the valence and conduction bands are populated as well as the Fermi energy. When the Fermi level is at or above the bottom of the conduction band, protons become highly mobile.

We would like to suggest that it is possible to produce a protonic semi-conductor analogue of this device. Further, as for a two dimensional electron gas, the density of energy states is a constant and the Fermi energy is proportional to the hydrogen atom density. Therefore, hydrogen density in the inversion layer increases with the strength of the applied potential and the kinetic energy of the hydrogen atoms increases more rapidly than Coulomb potential energy. It may therefore be possible to "tune" the occupation of the conduction band states so as increase the possibility of inelastic scattering due to matching lattice and nuclear states such as suggested by [11] in relation to a possible theory of the "cold fusion" phenomena.

The same two-dimensional effect is also expected in the so-called electrical double-layer central to much of electrochemistry. Bockris and Reddy [3] provide a detailed discussion of the structure of the electrical double-layer at the electrode-electrolyte interface. It may come as a surprise that there is considerable similarity between the charge distribution in MOSFETs and the structure of the double-layer. As a result we expect that the protons trapped in the approximately linearly varying electric field of the double-layer will have dynamics similar to the two-dimensional proton gas.

Good two-dimensional proton conduction and possible cold fusion effects have been reported in some crystal structures such as sintered oxygen deficient oxides $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ [12], hydrogen uranyl phosphate $HUO_2PO_4 \cdot 4H_2O$ (HUP), and hydronium β'' -alumina. Hydronium β'' -alumina [4] is prepared by ion exchange in concentrated sulfuric acid with sodium β'' -alumina. Despite the β'' - designation, β'' -alumina is not new crystalline form of alumina, rather it is a compound in which

consists of a structural backbone of close-packed $Al - O$ "spinel blocks" connected by $Al - O - Al$ columns with intervening ions such as Na^+ or H_3O^+ . Sodium β'' -alumina is also a good sodium ion conductor.

6 Conclusions

The possibilities for constructing devices that utilize the protonic semi-conductor properties of water and similar materials seem numerous. In particular, the quantum mechanical properties of hydrogen nuclei confined to a two-dimensional surface created by a potential gradient may give rise to novel proton/deuteron transport properties. These might include the possibility of matching lattice resonant states with nuclear states resulting in cold fusion.

The close analogy between electronic semi-conductors and protonic semi-conductors (as exemplified by aqueous electrolytes) makes it possible to transfer much of the enormous literature and theoretical results on semi-conductors to the behavior of protons in solution. This may well be a new and very fruitful area of research.

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