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Περί του στοιχείου του ύδατος or Deductive Molecular Mechanics of Crystalline Water

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Abstract. The deductive molecular mechanics (DMM) directly expresses the energy of a system of atoms in terms of the chemical bonds built upon hybrid atomic orbitals. Here we apply it to write down the total energy of the most symmetric crystalline water polymorph – ice X and to study its stability with respect to transition to the paraelectric ice VII with partial occupancy of hydrogen position and/or to the antiferroelectric ice VIII and the transition between the two latter phases. On this route we could establish several statements which can be qualified as theorems of DMM about ices. Further application of the proposed approach can eventually lead to the analytic description of the entire phase diagram of crystalline water (ices)

Introduction

In chemistry it goes about *elements* that is στοιχεία. As Aristotle transmits to us: “Θαλής μὲν ο τῆς τοιαύτης ἀρχηγός φιλοσοφίας ... ὕδωρ ἀρχὴν τῆς φύσεως εἶναι” [1]. Thus we address this time water like previously we addressed fire [2]. When it comes to water we recollect Ἡράκλειτος who said once “Πάντα ρεῖ”. Everything fluent is difficult to capture thus we consider ices.

Ice possesses extremely sophisticated phase diagram. Considering one given *e.g.* in [3] we notice that (i) frontiers between ices of different density are “horizontal” (Θ -independent); (ii) order-disorder frontiers are all “vertical” (Π -independent) except the VII/VIII boundary. The key to understanding order/disorder boundaries is the residual entropy: $\Delta S = \ln \frac{3}{2}$ [4] for the structures conforming to the ice rules [5], yielding the transition temperature:

$$\Theta_c(\Pi) = \frac{\Delta E(\Pi)}{\Delta S}.$$

Then pressure independent ordering energies ΔE explain the vertical boundaries, whereas the pressure dependent ones tentatively explain the pressure dependent (VII/VIII) one. Thus, the key problem is to describe the nonmolecular ice X and molecular ices VII and VIII uniformly. Otherwise, different approximations are used above and below X-VII/VIII boundary making any understanding impossible. Currently, a uniform description of water and its isomers is done on the basis of the DFT, although, the question “How good is DFT for water?” is still under discussion [6]. Irrespective to the answer the DFT results are obtained with use of ‘electronic computers’ [7]. Although such results are useful as all data obtained in a (numerical) experiment, no insight can be obtained on this path. Thus we undertake this study using the deductive molecular mechanics (DMM) [2, 8, 9, 10, 11, 12] directly addressing the relevant physics.

DMM model for ice energetics

DMM [2, 8, 9, 10, 11, 12] is based on the electronic wave function of a system taken as an antisymmetrized product of electronic groups [13] representing its observable parts combined with considering the shape and orientation of hybrid

orbitals (HO's) as independent variables of electronic structure (more details in [14, 15]). Previous attempts of performing the energy optimization with respect to these variables were sporadic (see e.g. [16]); we do it systematically. In this setting the energy of an ice in a “diamond like” structure is the sum of (i) H-bond energies - chemical (local) terms; (ii) energies of the O-atoms with hybrid AO's (HO's) and H-atoms - one-center terms; (iii) of their Coulomb (long-range) interactions. Each O atom is involved in 4 hydrogen bonds: of which two are short and two are long OH-components (ice rules !), thus per O atom *vis* H₂O molecule we have two OH bonds: one short and one long.

H-bond energies. One-electron hopping between HO's of two H-bonden oxygens and 1s of binding hydrogen produces:

$$-4B_s t_s - 4B_l t_l \quad (1)$$

where B_s , B_l are the Coulson spin bond orders for, respectively, short and long OH bonds; t_s , t_l are respective one-electron hopping (resonance) integrals. Coulomb interaction between electrons in oxygen HO's and those in 1s of hydrogen is:

$$2\gamma_{lh} (\Gamma_{lh}^{(+)} + \Gamma_{lh}^{(-)} - 2P_h P_l) + 2\gamma_{sh} (\Gamma_{sh}^{(+)} + \Gamma_{sh}^{(-)} - 2P_h P_s)$$

Γ 's are the elements of 2-RDM's for the respective OH bonds. In the SCF approximation 2-RDM's decouple which gives an effective “exchange” interaction:

$$-2(\gamma_{lh} B_l^2 + \gamma_{sh} B_s^2). \quad (2)$$

One-center contributions. *One-center repulsions.* At the CNDO level [17] these are intra-O electron-electron interactions between the densities residing in the HOs ascribed to different H-bonds incident to the same O-atom: $2g [P_s^2 + 4P_l P_s + P_l^2]$; and those inside the same HO: $2g [\Gamma^{ss} + \Gamma^{ll}]$. In the SCF approximation Γ 's decouple: $\Gamma^{ss} = P_s^2$, $\Gamma^{ll} = P_l^2$. H-intraatomic Coulomb repulsion (two per H₂O molecule) amounts: $2h\Gamma_{hh}$ where $h = (hh | hh)$, which in the SCF approximation yields: $2hP_h^2 = \frac{1}{2}h(1-q)^2$ (q is net charge of the H-atom).

Oxygen and Proton core attractions Core attraction to the proton is the simplest: $-2H(1-q)$, whereas the O-core attraction: $-4(U_s P_s + U_l P_l)$ involves the hybridization dependent core-attraction matrix elements: $U_{s,l} = U_{pp} + (U_{ss} - U_{pp}) s_{s,l}^2$ with s 's - 2s-AO coefficients in the respective O-HO's parameterized as: $s_{s,l} = \frac{1}{2}(\cos \varsigma \mp \sin \varsigma)$.

Long-range interactions. Long-range Coulomb terms yield the structure dependent contribution: $-mq^2 R^{-1}$ expressed through the shortest anion-cation separation R and the Madelung constant $m_{\text{Cu}_2\text{O}} = 4.442$ (Cu₂O - structure type of ice X) [18, 19]. At the CNDO level [17] the divergence of this term is lifted by distinguishing Coulomb repulsion of atomic cores $\propto R^{-1}$, attraction of electronic cloud to an alien core $\propto V(R)$, repulsion between the clouds on different atoms $\propto \gamma(R)$ and setting $V(R)$ equal to $\gamma(R)$:

$$Z_1 Z_2 (R^{-1} - \gamma(R)) + Q_1 Q_2 \gamma(R)$$

with the effective charges $Q_i = Z_i - P_i$. Bracket at $Z_1 Z_2$ is an exponentially decaying “Yukawa” potential $Y(R)$. Since $\gamma(R) \propto R^{-1}$; $R \rightarrow \infty$ we replace $\gamma(R)$ by R^{-1} for all pairs except nearest neighbors: four H-atoms interacting with (i) an O atom: $-4q^2 \gamma_{\text{OH}}(R \pm r)$ (both signs are used); (ii) among themselves: $q^2 \gamma_{\text{HH}}(R_{mm'})$ at the distances R_{ss}, R_{ll}, R_{ls} between H-atoms on the short and long OH-bonds. Separating the contribution of the nearest neighbors reduces the Madelung constant by $m_{\text{NN}} = 8 - 3\sqrt{\frac{3}{2}} \approx 4.326$. Thus the long-range energy is $-\mu q^2 R^{-1}$ with $\mu = m - m_{\text{NN}} \ll 1$.

Parity. The energy contributions all have the form:

$$-(a_s b_s + a_l b_l) \quad (3)$$

and possess a kind of “pairity”. The whole thing evolves around the question whether the minimum of the sum of such quantities refers to equal values of the quantities with different subscripts or not. In the symmetrized components $A, a, B, b, \dots$:

$$\begin{aligned} b_s &= B + b; b_l &= B - b \\ a_s &= A + a; a_l &= A - a \end{aligned}$$

the energy of *whatever* ice-rules conforming phase is:

$$\begin{aligned}
& -8(BT + bt) - 4[(\gamma_{lh} + \gamma_{sh})(B^2 + b^2) + 2(\gamma_{sh} - \gamma_{lh})Bb] \\
& -8(UP + up) - 8H(1 - P) + 4g(7P^2 - p^2) + 8h(1 - P)^2 \\
& -4q^2\gamma_{OH}(R \pm r) + q^2[\gamma_{HH}(R_{ss}) + \gamma_{HH}(R_{ll}) + 4\gamma_{HH}(R_{ls})] - \frac{\mu q^2}{R} \\
& + 12Y_{OH}(R \pm r) + [Y_{HH}(R_{ss}) + Y_{HH}(R_{ll}) + 4Y_{HH}(R_{ls})] + \Pi\Omega R^3
\end{aligned} \tag{4}$$

per H₂O molecule (here we complemented the energy by the hydrostatic term). Its symmetric minimum corresponds to vanishing "small" characters b, r, p in eq. (4).

Quantum chemical consideration of H-bond yields the the orbital populations, H-atom charge, and the OH bond orders P, p, q, B, b in eq. (4). H-bond is a specific case of the 3-center-4-election bond. Generalizing [20, 21], the vacant MO (with two nodes) through the l -, h -, and s -orbitals belonging to an H-bond is:

$$|V\rangle = \left(-\sin\varphi \sin\frac{\vartheta}{2}, \cos\varphi, -\sin\varphi \cos\frac{\vartheta}{2}\right) \tag{5}$$

The angles φ and ω ($\vartheta = \frac{\pi}{2} + \omega$) parameterize the subspace of the occupied MO's orthogonal to $|V\rangle$ and express density elements B, b, P, p, q . Finally, the HOH angles when vary in the vicinity of the tetrahedral one $\Theta_{ss,ll} = \arccos(-\frac{1}{3}) \mp \Phi$ are controlled by the single geometry variable Φ .

Theorem about ice X

The energy eq. (4) describing whatever ice conforming to the ice rules is a function of $R, \varphi, r, \varsigma, \omega, \Phi$. Each in the collection of the contributing terms is an *even* function of $r, \varsigma, \omega, \Phi$:

$$E(R, \varphi, r, \varsigma, \omega, \Phi) = E(R, \varphi, -r, -\varsigma, -\omega, -\Phi)$$

Whatever such function has vanishing partial derivatives with respect to *invertible* variables at their zero values. These define the "ice X" manifold as well dubbed as "symmetric H-bond". This immediately leads to the *mathematical* conclusion that a stationary point of the energy functional with respect to remaining variables R, φ in this manifold is the sought stationary point with respect to *all* variables.

Symmetric H-bond. In it only one electronic variable $q = \cos 2\varphi$ (H-charge) survives. This considerably simplifies (all uncapitalized quantities in eq. (4) vanish and the symmerized OH-bond order expresses through the H-charge $B = \sqrt{(1-q^2)/8}$) the description. Furthermore, the resonance term expands: $\sqrt{1-q^2} \approx 1 - \frac{1}{2}q^2 - \dots$ making the energy of the symmetric H-bond merely a quadratic function of q :

$$\varepsilon_X(R, q) = \left(\mathfrak{C}_0(R) - \frac{\mu_X}{R}\right)q^2 + \mathfrak{B}q + \left(\mathfrak{U}_0(R) + \Pi\Omega_X R^3\right)$$

where $\mathfrak{U}_0(R), \mathfrak{C}_0(R)$ are some known combinations of the "Yukawa", two-center Coulomb and resonance, and one-center contributions. Remarkably, $\mathfrak{B} = 2(H - U) - h + \frac{21}{2}g$ does not depend on R and the structure specific additives $\propto \mu_X$ and $\propto \Pi\Omega_X$ are some small corrections discussed below. The result optimizes with respect to q , yielding

$$\begin{aligned}
q_0^*(R) &= -\frac{\mathfrak{B}}{2\mathfrak{C}_0(R)} \\
\varepsilon_0^*(R) &= \mathfrak{U}_0(R) - \frac{\mathfrak{B}^2}{4\mathfrak{C}_0(R)}
\end{aligned}$$

- the equilibrium value of charge and the energy profile against the OH separation. Optimizing the energy profile against R yields the equilibrium OH separation $R_{\min}$ independent on the "global" structure. This proves the announced theorem: the energy restricted to the "ice X" - symmetric manifold *has* a minimum with respect to R (and q or φ). Moreover, the energy $\varepsilon_0^*(R_{\min})$ linearly depends on equilibrium value of H-charge as numerically found in [22].

Stability of ice X. The existence of ice X phase assumes the convexity of the energy function(al) in the symmetric extremum: the matrix of its second derivatives with respect to *all* variables $R, \varphi, r, \zeta, \omega, \Phi$ calculated in the “ice X” ($r = \zeta = \omega = \Phi = 0$) minimum with respect to R, φ - an ice X structure - must be positively definite. The 6×6 matrix of the Hessian breaks into 2×2 block (resp. R, φ) and 4×4 one (resp. to r, ζ, ω, Φ). The 2×2 block is positive definite for all accessible values of $R_{\min}$. The lowest eigenvalue of the 4×4 block turns negative at $R_{\min} \gtrsim 2.5a_0$ or $\Pi \lesssim 61$ GPa (the latter value is obtained for $\mu_X = 0.116, \Omega_X = {}^{32/3}\sqrt{3}$).

Ca. 88% of the weight of the eigenvector of the lowest eigenvalue lays in one component making the “long” and “short” components of an H-bond asymmetric. The corresponding second derivative $E''_{\omega\omega} = \sqrt{\frac{1-q^2}{2}}T - \frac{g}{2}(1-q)^2$ contains two terms: (i) *positive* distance dependent comes from OH-resonance; (ii) *always negative* distance independent comes from intra-O e-e repulsion. Changing Π or Ω and μ moves the minimum position $R_{\min}$ and affects the resonance integral T which turns to be small for larger $R_{\min}$ ’s and gets overridden by the negative intraatomic term and off-diagonal contributions ($E''_{\omega\omega}$ itself never gets negative).

Below X-VII/VIII critical pressure r, ζ, ω, Φ become nonvanishing, and optimal values of $R_{\min}$ and $q_{\min}$ also change. Distortions cause some asymmetry of charge distribution. From the point of view of other distant charges an effective dipoles $d_{\text{eff}} = \frac{4q}{\sqrt{3}}\left(r - \sqrt{2}R \sin \frac{\Phi}{2}\right)$ appear at each O atom and they interact. In the disordered ice VII average dipole-dipole interaction vanishes [23]. In the ordered ice VIII it is pressure dependent yielding the pressure dependence of the VII-VIII transition temperature: $\Theta_c = \frac{\kappa d_{\text{eff}}^2}{R^3 \Delta S}$ (κ is a constant characteristic for the lattice). In the detailed phase diagram [24] $\Theta_c \rightarrow 0$ ($r \rightarrow 0, \Phi \rightarrow 0$) provided $\Pi \nearrow \Pi_c \approx 62$ GPa. The triple point of ices VI, VII, and VIII (2 GPa, 944 K) yields the maximal accessible interaction energy estimated with use of $\Delta S = R \ln \frac{3}{2} = 3.371 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$. Our calculation yields 3 mHa *i.e.* 937 K.

Global structure effect. We studied the energy of “ex situ” symmetric H-bonds independent on the *global* structure and pressure ($\mu = \Pi = 0$). These quantities control two additives to $\varepsilon_0^*(R)$: (i) a pressure dependent term always increasing the energy, but tending to shift the $R_{\min}$ towards shorter separations (Ω is a factor coupling the molar volume with the cube of the half of O...O separation). It makes denser phases preferable at higher pressures and vice versa; (ii) μ produces either stabilizing and attractive, or destabilizing and repulsive, correction to the total depending on whether the contribution of not nearest neighbors to the Madelung sum is negative or positive. One more additive $\propto \kappa$ is characteristic for ordered phases.

We compared numerically the energies of the structures derived from β -cristobalite - ice Ic, and β -tridymite - ice Ih, having, respectively, a larger $\mu_{\text{Ic}} = 0.128$ and a smaller $\mu_{\text{Ih}} = 0.114$ reduced Madelung constants than that of ice X ($\mu_X = 0.116$). Increasing μ reduces energy for all pressures. Increasing Ω by 10% against ice X produces a transition at ca. 0.717 GPa disfavoring the potentially more stable ice Ic phase above this pressure. On the other hand, increased $\Omega = 1.79 \cdot \Omega_X, \kappa = 1.1$ (first from $\rho_{\text{VII}}/\rho_{\text{XI/I}}$, second is a plausible guess) makes ice XI (ordered ice Ih) more stable than ice VIII below 1.3 GPa.

Conclusion

Under ridiculously simple assumptions general energy expression valid for various crystalline water polymorphs is derived. It covers the range of pressures from 0 to 100 GPa. The existence of ice X polymorph is mathematically proven and the boundary of its stability vs. transition to “molecular” forms of ice VII and VIII is established. The intimate nature of this instability is clarified. The unique curvilinear form of the order/disorder phase boundary between ices VII and VIII is reproduced and understood. The low pressure region of the phase diagram is shown to be tentatively reproducible with use of global structure variables.

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