

Fractional Exclusion Statistics and the Broken Third Law of Thermodynamics: Its Implication to the Conjecture of Berry's Phase in Crystalline Ice

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The crystalline ice is known to have the "residual entropy" in the low temperature limit. We show that the residual entropy of ice may be reformulated in terms of the fractional exclusion statistics of Haldane at $T = 0$ with the statistical interaction parameter $\alpha = 0.867$. In other words, the fractional exclusion at $T = 0$ implies the broken third law of thermodynamics. Then the question arises whether the chemistry-driven fractional exclusion statistics in ice has anything to do with the topology-driven anyon (fractional phase) statistics as in the case of the quasi-particles in FQHE. In the present study, we perform electronic structure calculations for ice in order to probe the Born-Oppenheimer energy surface. We find the possibility that there exist Berry's phase contributing to the residual entropy (macroscopic ground-state degeneracy), establishing the connection between the fractional exclusion and the fractional phase.

It is well known that there exists residual entropy in ice, which fact has long been confirmed by many experiments [1-4]. The residual entropy was obtained by performing heat capacity measurements of ice down to 0.2 K [1], and its value is 0.82 cal./mol-K for hydrogen oxide [2] and 0.77 for deuterium oxide [3]. By assuming a random distribution of hydrogen bonds within the constraint of the so called ice rule, Pauling estimated the entropy as 0.806 cal./mol-K. Although this idea is purely classical, the agreement with experiment is excellent. A more sophisticated series expansion method yielded 0.815 cal./mol-K [5] in even closer agreement with the experimental value for the hydrogen oxide (i.e., the ordinary ice).

From a theoretical point of view, the existence of finite residual entropy means the broken third law of thermodynamics, posing a question whether there may exist a fundamental symmetry principle (or a violation of it) related to the broken third law in ice. In a previous paper published elsewhere [6], we showed that the residual entropy of ice may be reformulated in terms of fractional exclusion statistics of Haldane [7] in the $T = 0$ limit with the calculated statistical interaction parameter $\alpha = 0.867$. We estimated the potential barrier separating different energy minima in the Born-Oppenheimer energy surface for the hydrogen configuration space. The effective barrier height per hydrogen was $\lesssim 0.2$ eV, which is not large at all. Then we addressed the puzzle that, if different energy minima are separated by finite barriers, the macroscopic degeneracy of the energy minima would be lifted by quantum mechanical tunneling and the true (quantum-mechanical) ground state, being a linear superposition of these states localized in respective energy

minima, should be nondegenerate in energy. It would imply the absence of the residual entropy, in contradiction to the experimental observation of it. The resolution we proposed to overcome this conceptual dilemma was that there may arise Berry's phase [8] in ice. If Berry's phase should exist in the electronic structure of ice, the macroscopic degeneracy could be explained in terms of the well-known ground-state degeneracy (corresponding to a nonzero 'pseudo' angular momentum of the ground state) in the presence of Berry's phase. For Berry's phase to appear, it is necessary that the trajectory of the ionic configuration (the slow variable) encloses a point (in the hydrogenic configuration space) at which the corresponding electronic states (the fast variable) are degenerate. Now it is extremely desirable to do realistic calculations to obtain a more convincing value for the barrier height as well as the precise hydrogenic configuration at which the electronic states are degenerate. In the first half of the present paper, we will review the relation between the fractional exclusion statistics and the broken third law of thermodynamics in crystalline ice. This part has been published in Ref. 6. In the latter half of it, we will present the results of our recent calculations on the barrier height separating energy minima and the hydrogenic configuration that may give rise to Berry's phase $\gamma = \pi$ locally, hence contribute to the macroscopic overall ground-state degeneracy of order a^N ($a > 1$). We will first outline below the existence of finite residual entropy in ice and the reformation of it in terms of the fractional exclusion statistics.

The stable structure of ice at low temperatures is known to be hexagonal and each oxygen atom is surrounded by four nearest-neighbor oxygen atoms. There

are two chemical constraints for the hydrogenic configurations, namely, (1) that there be one hydrogen atom between any pair of neighboring oxygen atoms and (2) that there be two hydrogen atoms near to (and two hydrogen atoms away from) a given oxygen atom. Consequently, the local configuration around an oxygen atom in ice is H_2O -molecule-like. For convenience in presentation, we assume that the first constraint is already satisfied by the stoichiometric (H_2O) ice (violation of which would cost too much energy), and we will from now on call the second constraint as the ice rule. In general, a hydrogen atom located between oxygen atoms I and II can occupy either one of two equilibrium sites, one near to atom I (site A) and the other near to atom II (site B). Therefore, before the ice rule is imposed, the total number of possible hydrogenic configurations is 2^{2N} , where N is the number of oxygen atoms which sets the system size. It was a famous problem in statistical mechanics to count the number of different configurations satisfying the ice rule in the thermodynamic (large N) limit, and the answer [5] turned out to be $\sim 1.507^N$.

Now we can map the statistics of the hydrogenic configuration under the ice rule onto the fractional exclusion statistics. The situation of the maximal degeneracy (2^{2N}) in the absence of the ice rule is mapped to the bosonic statistics, complete vanishment of the configurational degrees of freedom to the fermionic statistics, and the intermediate (realistic) case to the fractional statistics. Following Wu's formalism [9], if there are N_p identical particles occupying G one-particle states of identical energy, the number of N_p -particle states (i.e., the degeneracy of the many-body system) W is

$$W(G, N_p, \alpha) = \frac{[G + (N_p - 1)(1 - \alpha)]!}{[G - \alpha N_p - (1 - \alpha)]! N_p!} \quad (1)$$

$\alpha = 0$ corresponds to bosons, $\alpha = 1$ to fermions, and $0 < \alpha < 1$ to particles of fractional statistics interpolating between the two limits. On the other hand, with use of the identity $2^{2N} = \sum_{m=0}^{2N} \binom{2N}{m}$ where $\binom{2N}{m} = 2N! / m!(2N - m)!$, the logarithm of the total number of states of ice for N oxygens *without* the ice rule in the thermodynamic limit would be

$$\begin{aligned} \ln \sum_{m=0}^{2N} \binom{2N}{m} &\approx \ln \binom{2N}{N} \\ &\approx \ln \binom{2N-1}{N} \end{aligned} \quad (2)$$

In the first line of Eq.(2), regarding m as the variable number of particles, we retain only the largest term in the summation in the spirit of the equivalence between the grand canonical ensemble and the canonical ensemble. (Or, we simply apply Stirling's formula.) In the second line, $\binom{2N-1}{N}$ may immediately be interpreted as the degeneracy of many-boson states when G (number of one-particle states) = N and N_p (number of particles) = N .

With $G = N_p = N$, the number count for a frozen-in state having no configurational degrees of freedom is trivially $\binom{G}{N_p} = \binom{N}{N} = 1$, corresponding to the degeneracy of N fermions occupying N states. In other words, G and N_p of ice are uniquely determined under the two "boundary conditions", $W(G, N_p, 0) = 2N \ln 2$ and $W(G, N_p, 1) = 0$. Of course, $G = N_p = N$ corresponds to the case where the crystalline ice does not have any deficit or excess of hydrogen atoms or other defects in bonds. The configurational entropy of real ice is $kN \ln 1.507$, a value between the two extremes. α for ice is obtained by substituting $G = N_p = N$ in Eq.(1) (we neglect 1 compared to N whenever convenient) and comparing it with the residual entropy,

$$N \ln 1.507 \approx (2 - \alpha)N \ln(2 - \alpha) - (1 - \alpha)N \ln(1 - \alpha) \quad (3)$$

We obtain $\alpha \approx 0.867$. To recapitulate, two possible sites (A and B) for each hydrogen atom would be fully available if the presence of other hydrogen atoms in neighboring bonds would not restrict the freedom of choice between A and B (just as the presence of other particles does not restrict the availability of states in boson statistics), but other hydrogen atoms do impose some statistical constraint (i.e., certain, but not all, states become excluded) in reality and the measure of the constraint in ice is $\alpha = 0.867$. In this formulation, the basic requirement for the fractional exclusion statistics [7] is automatically satisfied: G (= N) is finite and extensive, proportional to the size of the condensed matter region because N is defined to be the system size.

We want to note that the "particles" in the fractional statistics are not necessarily *true excitations* of any kind. In the present case, we are counting the *ground-state* degeneracy of the N -particle system. The distinction is immaterial because the particles in the degenerate ground states may be regarded as being created from the null state just as excitations are created from the ground state. When the reduction of the degeneracy by the chemical constraint is converted into the statistics of the noninteracting particles of fractional α , the meaning of the "particles" and "one-particle states" becomes rather abstract. Suppose we assign A and B to two possible hydrogenic sites for every bond between oxygens as before. Any hydrogenic configuration of the whole system can be described by a sequence of A's and B's (with $2N$ of them in total) representing the sites actually occupied by hydrogens. Then we identify A with a "particle" and B with a "wall dividing one state from another" (so that the number of B's is equal to $G - 1$). The most probable values for the number of A's and B's are both N . We can easily check that aforementioned mapping to the fractional exclusion statistics is accomplished this way.

We have stated, in terms of the Born-Oppenheimer energy surface, that there are 1.507^N potential minima of equal well depth corresponding to ice-rule-satisfying con-

figurations. What we have so far neglected is the kinetic part, namely, the quantum mechanical tunneling and the corresponding energy-level splitting. Of course, the tunneling splitting of energy levels decreases as the barrier height increases and the states become practically degenerate. However, if the potential barrier becomes too high, a particular hydrogenic configuration is frozen in and other configurations are inaccessible. It was Ma [10] who correctly stated, on the question of the residual entropy of glasses, that "as $T \rightarrow 0$, motions stop and entropy also tends to zero. The third law (of thermodynamics) cannot be violated." The often-claimed residual entropy of glasses obtained by integrating C_p/T is an artifact of the irreversibility of the thermal process which causes the inequality

$$\int_0^T C_p/T dT < \Delta S (= S(T) - S(0)) . \quad (4)$$

This explains why the measured residual entropy of glasses is not unique or reproducible (sample- and history-dependent). The situation in the crystalline ice, however, is quite different. Careful experiment always produces the same residual entropy and it coincides precisely with the theoretically anticipated value. The crystalline ice, despite its random hydrogenic configuration, does not in general exhibit characteristics of glasses (e.g., glass transition, hysteresis, or frustration). If we regard $(\Delta S - \int_0^T C_p/T dT)$ as a measure of irreversibility, this quantity for ice must be negligibly small. In this context, we note Ma also mentioned in the same reference [10] that the residual entropy can be nonzero if the ground state is truly degenerate (as opposed to being frozen as in glasses). The measured residual entropy of ice is likely to reflect the truly accessible states down to the experimental temperature (0.2K). In combination with information available in the literature [11-13], we roughly estimated that the minimum barrier per hydrogen tunneling ~ 0.12 eV. (The actual calculations which give the upper bound of the minimum barrier height will be described in the latter half of the paper.) The corresponding tunneling time turns out to be $\sim 10^{-7}$ s. It means that, within the specific heat measurement time ($1 \sim 10^4$ s), tunneling can occur frequently to probe enough of the available configuration space.

It is ironic, however, that the very existence of quantum tunneling undermines the finite residual entropy. In the presence of quantum tunneling between potential minima, a new nondegenerate ground state is formed by the linear combination of these configurations with equal coefficients and the tunneling splitting of energy levels follows. (We want to emphasize that, at such a low $T \sim 0.2$ K we are in, the quantum tunneling rate is much greater than the thermal hopping rate and the coherent description of pure eigenstates is valid.) The estimated energy splitting should be greater than 0.1 meV, much too great to pass undetected in the specific heat measurement at 0.2K. In other words, accessibility to many potential minima

does not explain the finite residual entropy. To overcome this dilemma, we have made a rather unusual proposal, namely, that there appear Berry's phase in ice. A crucial point here is that the ice consists not only of nuclei but also of electrons. As protons move from one configuration to another, electrons follow protons' motion and the many-electron wavefunction changes as well. It has been proved in the literature that the electronic state (the fast variable) picks up Berry's phase $\gamma = \pi$ if the trajectory of the ionic configuration (the slow variable) encloses a point at which the electronic states are doubly degenerate. Such phenomena are known to occur at defects in crystals [14] or in Na_3 molecules [15]. Therefore, the finite residual entropy and the subsequent violation of the third law of thermodynamics in the practical sense are expected based on the existence of Berry's phase. But the question remains whether the energy barrier we have estimated from information in various literatures and our simple model calculation reflects the true minimum value. Furthermore, the existence of the hydrogen configuration at which the electronic states are degenerate is yet to be confirmed. The next half of our paper is devoted to the realistic calculations of the electronic and atomic structures of ice that gives us the upper bound of the minimum energy barrier as well as a hydrogenic configuration with doubly degenerate electronic states. These results provide supporting evidence for our conjecture of Berry's phase in ice.

The tunneling should occur primarily along the path with the minimum energy barrier, but essentially infinite degrees of freedom in hydrogenic motions prohibit us from determining the path unambiguously. Only upper bound of the minimum barrier height can be determined in practice. First, we take a very simple mode of tunneling in which all hydrogens translate simultaneously along

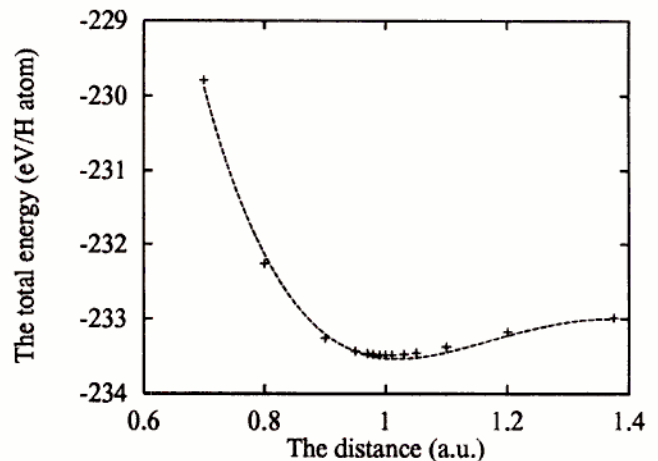


Fig. 1. Total energy curve with respect to the uniform translation of hydrogens in the cubic ice. The x -axis designates the distance between a hydrogen and its nearest oxygen.

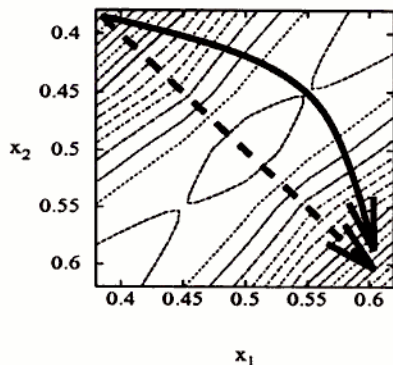


Fig. 2. The energy contour when two hydrogens in one water molecule move independently.

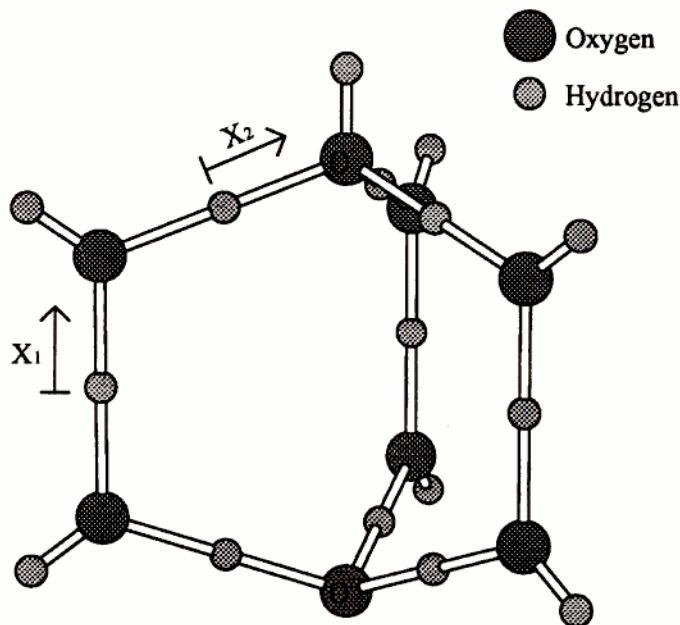


Fig. 3. The $6\text{H}_2\text{O}$ cluster studied here for the existence of Berry's phase.

the bonds towards respective oxygen atoms forming the hydrogen bonds (thus breaking the covalent bonds between each pair of hydrogen and oxygen atoms). We have performed *ab initio* pseudopotential calculations to obtain the Born-Oppenheimer energy surface for the translation. In order to reduce the computational load, the cubic ice with two H_2O molecules in the unit cell is studied. The experimental cell volume is used and only $\vec{k} = 0$ point is considered for the Brillouin zone integration. The gradient-corrected local density approximation is adopted since it is known to predict properties of the hydrogen bond correctly [16,1]. The functional form of Becke [18] is used in exchange energy, and that of Perdew [19] in correlation energy. This kind of choice was tested in the paper of Ortiz *et al.* [20]. We have adopted the partial core correction [21] to the oxygen atoms since the overlap between $1s$ and $2p$ electrons in oxygen atoms is not small. The resulting Born-Oppenheimer surface is plotted in Fig. 1. The line in the figure is the quartically fitted polynomial, $E(\text{eV}/\text{H atom}) = -233 - 8.5(x - 1.375)^2 + 33.66(x - 1.375)^4$ with x in the atomic unit. From this curve the frequency of the collective oscillatory motion of hydrogens around minimum is 0.38 eV i.e., 3064 cm^{-1} in wavenumber. This is in reasonable agreement with the experimental H-O stretching mode in ice of 3220 cm^{-1} [22]. The height of energy barrier is $0.48 \text{ eV}/\text{H atom}$ and when the zero point vibrational energy is taken into account, the actual barrier is reduced to $0.28 \text{ eV}/\text{H atom}$.

Of course, this is not the minimum barrier path available. In order to illustrate this point, we let the two hydrogens in the same H_2O molecule move independently. The resulting 2-dimensional Born-Oppenheimer surface is shown in Fig. 2. The x_1, x_2 is the properly scaled coordinates of the hydrogens so that the lower right or upper left corner corresponds to the equilibrium position, and the central point corresponds to the configuration where all the hydrogens are in the middle of oxygens. The diagonal path (broken line) is the one calculated in the above. The curved path (thick line) is the more optimized one where the barrier height is lowered about $0.05 \text{ eV}/\text{H atom}$. It is certain that as more degrees of freedom are given the barrier will be lowered. We believe that a similar calculation for a single hydrogen tunneling [11] using the same method as ours gives a value close to the minimum barrier height for the collective motion. Unfortunately, the fully optimized relaxation of the environment and the precise collective tunneling made is far beyond the computational capability at present. The true zero-point-motion-corrected minimum barrier for the collective tunneling is believed to be close to $\sim 0.15 \text{ eV}/\text{H atom}$ in Ref. [11] and the mode we just calculated gives a value (0.23 eV) not too far above this. In any case, the barrier height is not insurmountably large, at least.

Now we want to face with the question of Berry's phase. We have proposed the existence of Berry's phase to resolve the puzzle in relation with the degeneracy in the

presence of quantum tunneling. The task here is to prove the existence of a hydrogenic configuration at which the electronic states are doubly degenerate. Since the degree of freedom in crystalline ice is unmanageably high, we rather choose a cluster made of eight H₂O molecules for simplicity. The structure of the cluster is shown in Fig. 3. The configuration of oxygen atoms in this figure is identical to a part of the oxygen lattice in hexagonal ice. In order to further simplify the analysis, we have considered only two degrees of freedom in hydrogenic motion which are denoted by x_1, x_2 in Fig. 3. The hydrogens at the same height in the figure move in an identical way and the symmetry group of the whole cluster is always preserved. The seven hydrogens extruding outward are fixed relative to oxygens with the typical equilibrium O-H length and the three basal hydrogens located between oxygens at the bottom are fixed in the middle position between oxygens. The relative coordinates x_1 and x_2 are determined as

$$x_i = \frac{d(\text{O} \cdots \text{H}) - 0.5 \times d_0}{d_0}, \quad (5)$$

where d_0 is the equilibrium O-O distance and $d(\text{O} \cdots \text{H})$ represents the distance of H from the lower O as indicated in the figure. We have performed *ab initio* pseudopotential calculations for the commonly used supercell geometry in order to obtain the energy levels of the cluster. The structure of the supercell containing the cluster is a simple cubic with lattice constants of 16 a.u. and only the $\mathbf{k} = 0$ point is considered in the Brillouin zone integration. In order to minimize the (undesirable) interactions between the clusters, O-O' axis in Fig. 3 is set to lie in the (1,1,1) direction. In this case the minimum distance

Table 1. Band gap(eV) as a function of x_1 and x_2 . For practical reasons, not all entries are calculated.

$x_1 \setminus x_2$	0.0	0.1	0.2	0.33
0.0	2.1	-	-	-
0.1	1.4	1.0	0.5	-
0.2	0.8	0.5	-	-
0.33	0.5	-	-	-

Table 2. Total energy (eV) as a function of x_1 and x_2 . For practical reasons, not all entries are calculated.

$x_1 \setminus x_2$	0.0	0.1	0.2	0.33
0.0	0.0	-	-	-
1.4	2.9	3.3	9.2	-
2.8	9.5	9.5	-	-
4.5	102.0	-	-	-

between hydrogens in different cells is 6.3 a.u., that between oxygens 8.2 a.u., and that between hydrogen and oxygen 6.8 a.u.. All these lengths are much greater than typical bonding distances. This means that the overlap between electrons in different cells is negligible, but the electrostatic interaction between supercells may still be substantial. For more quantitative confirmation, we have compared the energy levels with those in a larger supercell with the lattice constant of 19 a.u. and noted that all energy levels shift rigidly by the same amount. Since only the differences between energy levels are relevant for the present purpose, the remnant electrostatic interactions between supercells do not pose a problem here.

The band gap and the total energy as a function of x_1, x_2 are shown in Tables 1 and 2. The total energy is measured with respect to $x_1 = x_2 = 0$. The calculated band gap in ice is about 4 eV. From the table, one can see easily that as x_1 and x_2 get closer to 0.5 the gap becomes smaller. When the band gap becomes too small, we could not obtain the converged result because single \mathbf{k} point scheme is insufficient for such a metal-like system. However, there is no doubt that the gap will collapse to zero at some x_1 and x_2 and the degeneracy of electronic states will follow. In addition, it can be inferred from the table that the x_2 coordinate of the collapsing point is a function of x_1 , which implies that the singular (degenerate) points form a "string" in the x_1, x_2 plane.

Now we want to estimate the energy difference between the ground state and the singular point. The purpose of estimating this value is that the singular point should be sufficiently high in energy so that the hydrogen configuration corresponding to this singular point may not actually be accessible. (This is in fact another necessary condition for Berry's phase to realize [8].) As stated previously, the calculated energy barrier in cubic ice is ~ 0.2 eV per H atom. The total energy difference (corresponding to movements of six hydrogens) between the singular point and the configuration where $x_1 = x_2 = 0$ is more than 9 eV (or, 1.5 eV per hydrogen) in Table 2, at least. Adding these two values, we obtain at least 1.7 eV/H atom, which means the singular point is inaccessible and the necessary condition for Berry's phase is satisfied.

In the example of the defects or Na₃ molecules [14,15], the pseudo angular momentum is quantized as $\frac{1}{2}$ due to Berry's phase and the ground state becomes doubly degenerate like a spin-half system. Even though the presence of a singular point is not a sufficient condition for Berry's phase, we conjecture that a similar phenomenon as in defects or Na₃ molecules would occur in this structural part of crystalline ice and eventually gives rise to finite residual entropy for the bulk ice.

In summary, we have shown that the residual entropy of ice may be interpreted as a realization of the fractional exclusion statistics in three spatial dimensions. The experimental observation of the residual entropy suggests that a macroscopic number of degenerate configurations may actually be accessible even at low temperatures through

quantum tunneling. Occurrence of quantum tunneling, however, normally causes an appreciable energy level splitting which would in turn make the residual entropy vanish, leaving us in a paradoxical situation. We propose that the emergence of Berry's phase through the topologically nontrivial, collective tunneling of hydrogen atoms can resolve this puzzle and explain the finite residual entropy. To support this proposal, we have performed *ab initio* pseudopotential calculations on the cluster of eight water molecules resembling the structure of the hexagonal ice and found that electronic ground states can become degenerate for a certain hydrogenic configuration. We conclude that the topological excitation may be an essential feature of the fractional exclusion statistics even in the case of ice where the chemical constraint is the source of such exclusion.

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