Electromagnetism on ice: classical and quantum theories of proton disorder in hexagonal water ice

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Water ice is at once one of the most ubiquitous, and one of the most mysterious materials on Earth, displaying no less than 17 different crystalline structures. In the most common, hexagonal (Ih) form of ice, only oxygen (O²⁻) ions form an ordered lattice, while the protons (H⁺) remain disordered. These disordered proton configurations are subject to the Bernal–Fowler “ice rules”, which impose a zero–divergence condition on the local polarisation of the crystal, in close analogy with electromagnetism. Recent neutron scattering experiments further suggest that protons in hexagonal water ice remain mobile at the lowest temperatures, tunnelling from one configuration obeying the ice rules to another [Bove et al., Phys. Rev. Lett. 103, 165901 (2009)]. In this article we revisit the theory of correlations in proton–disordered Iₜ water ice, developing the existing analogy with electromagnetism into a complete and quantitative theory. We construct both a classical theory of static proton disorder, and a quantum theory in which protons tunnel collectively from one disordered ice configuration to another, making explicit predictions for neutron and X–ray scattering experiments in both cases. In the classical case, taking proper account of the symmetries of the Iₜ lattice, we find that proton correlations are governed by two distinct fields, one with power–law, and one with exponential correlations. The predictions of this classical field theory are shown to be in good agreement with classical Monte Carlo simulations, with an analytic calculation based on projection onto states obeying the ice–rules, and with published neutron scattering experiments on hexagonal water ice. In the quantum case, we show that proton correlations can be described using a compact, frustrated U(1) lattice–gauge theory, in which the low–energy excitations of protons have the character of “photons”. Exactly like light in hexagonal water ice, these emergent photons are birefringent, exhibiting a dispersion which depends on both the direction of propagation and polarization of the photon. The predictions of the quantum theory are shown to be in quantitative agreement with the results of quantum Monte Carlo simulations of hexagonal water ice, and to reproduce the “wings” of incoherent inelastic neutron scattering observed by Bove et al. These results raise the intriguing possibility that the protons in hexagonal water ice could form a quantum liquid at low temperatures, in which protons are not merely disordered, but continually fluctuate between different configurations obeying the ice rules.

I. INTRODUCTION

We learn as children that matter can exist in three different phases — solid, liquid, and gas. This concept is usually introduced through the example of water, familiar as a liquid (water), a gas (steam) and a solid (ice). However, at least as far as its solid phase is concerned, water is a spectacularly unusual material. At atmospheric pressure, water molecules freeze into a structure known as “water ice”, illustrated in Fig. 1. Ice Ih is remarkable in that the oxygen ions (O²⁻) form an ordered lattice, while the protons (H⁺) lack any kind of long–range order — in flat contradiction with the usual paradigm for solids.

This extraordinary property of water ice was first elucidated more than 80 years ago, by Bernal and Fowler [1]. Bernal and Fowler argued that ice should be viewed as a molecular solid, in which distinct water molecules are bound together by hydrogen bonds. Each water molecule forms four such hydrogen bonds, and as a result, the proton configurations obey strong local constraints, commonly referred to as the “ice rules” [1,2]. The ice rules lead to strong correlations between protons, but can be satisfied by an exponentially large number of different proton configurations [2,3]. As a result, the protons remain disordered, and possess an extensive residual entropy. This “ice entropy” is observed in experiments on Ih water ice [4,5], and persists down to the lowest temperatures measured, in apparent defiance of the laws of thermodynamics. Eighty years on, these striking discoveries continue to exert a profound influence on research into water ice [6], and a wide range of other materials [7,17].

Recent experiments by Bove et al. [18] suggest a new twist on the behaviour of protons in Ih water ice — not only are protons disordered, but they remain mobile, even at temperatures as low as 5 K. This might seem surprising, since any attempt to move a proton will lead to a violation of the ice rules, at considerable cost in energy [6]. This problem is avoided, however, if the proton dynamics consists of coherent quantum tunnelling on hexagonal plaquettes, of the type illustrated
FIG. 1. (Color online). Crystal structure of hexagonal (Ih) water ice. Water ice can be viewed as a frozen configuration of water molecules, satisfying the Bernal–Fowler “ice rules” [1,2], in which each oxygen (red sphere) forms two short, covalent bonds, and two long, hydrogen bonds with neighbouring protons (white spheres). Oxygen atoms form an ordered lattice, belonging to the hexagonal space group P6₃/mmc, with a 4–site primitive unit cell. Protons do not show any long–range order. (a) Structure viewed perpendicular to the hexagonal symmetry axis (the crystallographic c-axis). (b) Structure viewed along the hexagonal symmetry axis.

FIG. 2. (Color online). Collective, quantum tunnelling between different proton configurations satisfying the ice rules in hexagonal (Ih) water ice. The crystal structure of Ih water ice contains two distinct types of hexagonal plaquette, each containing six oxygen atoms (white spheres). Tunnelling between different ice configurations is mediated by correlated hopping of protons (red spheres) around such a plaquette. Where protons form an alternating sequence of short (S) and long (L) bonds (e.g. S–L–S–L…–S–L), it is possible to tunnel to another, degenerate, ice configuration in which long and short bonds are interchanged, (i.e. L–S–L–S…–L–S) [18–20]. (a) Tunnelling on hexagonal plaquette of “type I”, in the plane perpendicular to the hexagonal symmetry axis. This process has a matrix element $g_1$ in our model for proton dynamics, $\mathcal{H}_{\text{tunnelling}}$ [Eq. (4)]. (b) Tunnelling on hexagonal plaquette of “type II”, connecting different hexagonal planes. This process has a matrix element $g_2$. 
in Fig. 2. This mechanism for proton dynamics in $Ih$ water ice finds support from $ab initio$ calculations \cite{19, 22}, with recent results suggesting that, while the high–temperature dynamics proceeds via single–proton hopping, collective motion around loops becomes important at low temperatures \cite{21}. And an analogous correlated tunnelling of protons has recently been observed in an artificial assembly of four water molecules \cite{16}.

There are, in fact, many classes of system whose low–temperature physics is subject to strong local constraints, similar to those found in water ice. The most celebrated of these are the magnetic systems known as the “spin ices”, whose low–temperature spin configurations are in correspondence with the proton configurations in water ice \cite{7, 8, 10}. However ice–like physics also arises in models of frustrated charge order \cite{12, 13}, proton–bonded ferroelectrics \cite{14, 15}, dense polymer melts \cite{23} and dimer models \cite{24, 25}. In these systems, violations of the ice rules take on the character of fractionalised charges \cite{13}. This point has attracted particular attention in the case of the spin ices, since these charges behave as effective magnetic monopoles \cite{26, 29}. And, in fact, a direct analogy may be drawn between these magnetic monopoles and ionic defects in water ice \cite{26, 30}.

The effect of quantum tunnelling, of the type proposed by Bove et al. \cite{18}, has been studied in a range of other ice–like problems, with striking results. Quantum tunnelling has been shown to give rise to a quantum “spin–liquid”, comprising a coherent superposition of an exponentially large number of states obeying the ice rules, in models derived from spin ice \cite{31, 37}. Equivalent quantum liquids have also been found in three–dimensional quantum dimer models \cite{38–40}. In both cases, the low–energy excitations of liquid are gapped, fractionalised, “charges” and gapless, linearly dispersing, “photons”, in direct correspondence with the theory of electromagnetism \cite{31, 38}.

A similar “electromagnetic” scenario has also been explored in a simplified model of water ice by Castro Neto et al. \cite{41}. The phase diagram proposed by these authors contained a deconfined \cite{42}, liquid, phase and a confined, proton–ordered, phase. They suggested that the quantum ground state of $Ih$ water ice belongs in the confining phase, with a phase transition occurring between the two phases at finite temperature.

In the work which we present here we do not attempt to establish the conditions under which the protons in hexagonal water ice order, but instead seek to characterise their deconfined, disordered phase. To this end we develop theories describing the proton correlations in both classical and quantum models of hexagonal ($Ih$) water ice, making explicit predictions for scattering experiments.

In the case of classical $Ih$ water ice, we find that a full description of proton configurations requires us to introduce two independent fields. One of these fields has power–law correlations, and controls the long–distance form of the proton correlations. The other field has exponentially decaying correlations, and influences the short–distance form of the proton correlations. The predictions of this classical field theory are shown to be in agreement with lattice–based calculations, developed in an Appendix, and with classical Monte Carlo simulations of classical $Ih$ water ice.

This analysis of the classical problem provides new insight into the combinations of pinch–points and broad features observed in experiment on $Ih$ water ice \cite{43, 44}, and makes explicit the differences between correlations in hexagonal water ice, and those found on the cubic lattice of metastable $Ic$ water ice, or spin ice. It also provides the starting point needed to construct a theory of $Ih$ water ice in the presence of quantum tunnelling.

In the case of quantum $Ih$ water ice, we find that it is possible to describe the proton configurations in terms of a lattice–gauge theory in which the connection with electromagnetism, long–implied by the ice rules, is made explicit. The deconfined, proton–liquid phase of this theory is shown to support two types of excitation — gapless, linearly–dispersing photons with birefringent character, and weakly–dispersing optical modes, corresponding to local fluctuations of the electric polarisation. The predictions of this lattice gauge theory are shown to be in quantitative agreement with the results of variational quantum Monte Carlo simulations.

Throughout our analysis we will emphasise the ways in which proton–correlations in hexagonal water ice differ from spin–correlations in cubic spin ice, paying particular attention to the new structure which arises in both the classical continuum field theory, and the quantum lattice–gauge theory.

The remainder of the Article is structured as follows:

In Section I we introduce a model of $Ih$ water ice which includes tunnelling between different proton configurations obeying the “ice rules”, and describe those aspects of the symmetry and geometry of the $Ih$ water ice lattice which are important for our discussion.

In Section II we develop a coarse–grained, classical field theory describing the correlations of protons in $Ih$ water ice, in the absence of quantum tunnelling, and compare this with the results of an equivalent, lattice–based calculation, developed in Appendix C. The two approaches are shown to agree in the long–wavelength limit. The lattice–based calculation is also used to make explicit predictions for scattering experiments on a $Ih$ water ice. These are summarised in Fig. 6. Comparison is made with published results for hexagonal water ice.

In Section III we develop a quantum $U(1)$ lattice gauge theory describing the correlations of protons in $Ih$ water ice, in the presence of quantum tunnelling. We construct the excitations of this lattice gauge theory, which include birefringent emergent photons, and make quantitative predictions for their signature in inelastic scattering experiments. Key results are summarised in Fig. 7 and Fig. 8.

In Section IV we conclude with a summary of results, and a discussion of their relevance to $Ih$ water ice, making explicit comparison to the neutron–scattering experiments of Bove et al. \cite{18}.

Technical aspects of this work, including comparison with classical and quantum Monte Carlo simulations, are developed in a series of Appendices.

Appendix A provides details of the $Ih$ water ice lattice and of the coordinate system used to describe it.
II. CLASSICAL AND QUANTUM MODELS OF HEXAGONAL (Ih) WATER ICE

The key to understanding the structure of water ice is the realization, due to Bernal and Fowler, that water molecules retain their integrity on freezing \[1\]. It follows that each oxygen remains covalently bonded to two protons, while at the same time forming two, weaker, hydrogen bonds with protons on neighbouring water molecules. In the frozen state, the oxygen atoms form an ordered lattice, held together by intermediate protons, each of which forms one long (hydrogen) and one short (covalent) bond with a neighbouring oxygen. This type of bonding favours a tetrahedral coordination of oxygen atoms, but does not select any one structure, with 17 different forms of ice crystal known to exist \[6\].

Hexagonal (Ih) water ice, illustrated in Fig. 1, is the most common form of water ice, formed at ambient pressure. In it, oxygen atoms form a crystal with the hexagonal space group \(P6_3/mmc\). This structure can be thought of as a set of buckled honeycomb lattices, composed of centre–symmetric bonds of the type shown in Fig. 3(a) and (b). These honeycomb layers are linked by mirror–symmetric bonds, parallel to the hexagonal symmetry axis, of the the type shown in Fig. 3(c) and (d). The two types of bond have almost exactly the same length, leading to a near–perfect tetrahedral coordination of oxygen atoms \[6, 45–48\]. The primitive unit cell of Ih water ice contains 4 oxygen atoms or, equivalently, 4 water molecules, with 8 associated protons. This should be contrasted with the 2–site primitive unit cell needed to describe the diamond lattice of oxygen atoms in cubic (Ic) water ice (space group \(Fd\bar{3}m\)), or its magnetic analogue, spin–ice \[49\].

While the oxygen atoms in Ih water ice form an ordered lattice, protons do not. The way in which water molecules bond together does not select any one proton configuration \[1\], but rather an exponentially large set of proton configurations, where \(N\) is the number of oxygen atoms (equivalently, water molecules) in the lattice \[2, 3\]. As a consequence, the protons do not show any long–range order. While unusual, extensive degeneracies of this type are by no means unique to water ice, occurring in “spin ice” \[8, 10\], problems of frustrated charge order on the pyrochlore lattice \[12, 13\], and in a wide range of problems involving the hard–core dimer–coverings of two– or three–dimensional lattices \[24, 25\].

The principles governing the arrangement of protons in water ice are neatly summarised in the Bernal–Fowler “ice rules” \[1, 2, 6\] :

1. Each bond between oxygen atoms contains exactly one proton.

2. Each oxygen has exactly two protons adjacent to it.

Since the ice rules define one of the simplest models with an extensive ground–state entropy, they have proved a rich source
of inspiration for statistical studies [3, 50, 51], particularly in two dimensions, where the corresponding “six-vertex model” can be solved exactly [52, 53]. Violations of the ice rules cost finite energy, and fall into two types. Violations of the first ice rule, double–loaded or empty bonds, are known as Bjerrum defects [56]. Violations of the second rule occur where a proton is transferred from one bond to another. Since it is energetically expensive to violate the ice rules, tunnelling should occur between different configurations which satisfy the ice rules. This can be accomplished through the collective tunnelling of a group of protons, on any closed loop within the lattice, where the associated flux “arrows” also form a closed loop, as illustrated in Fig. 4.

Where such a loop exists, it is possible to generate a second proton configuration satisfying the ice rules, simply by interchanging long and short proton bonds. This is equivalent to reversing the sense of all fluxes on the loop. The shortest loops for which this is possible in Ih water ice consist of six oxygen–oxygen bonds, as illustrated in Fig. 2. Quantum tunnelling of the form considered in this paper preserves the topological sector, since this is unchanged by any local rearrangements of protons which preserves the condition of local flux conservation. As a consequence, the conserved flux is elevated to the role of a quantum number [40]. We note that, since all of these properties follow from the topological structure of ice, they are independent of the mechanism by which quantum tunnelling occurs [1? ].

The effect of quantum tunnelling on loops of six bonds has previously been explored in the context of quantum dimer models on the diamond lattice [38–40], and of quantum effects in spin ice [31, 33, 35, 36]. These models have the same cubic symmetry, Fd3m, as Ih water ice, for which the shortest closed loop of bonds defines the edge of an hexagonal plaque. Since all such plaquettes are related by lattice symmetries, a minimal model for quantum tunnelling can be obtained by introducing a single tunnelling matrix element $g$

$$\mathcal{H} = -g \sum_{\mathcal{O}} [ | \mathcal{O} \rangle \langle \mathcal{O} | + | \mathcal{O} \rangle \langle \mathcal{O} | ] ,$$

where the sum on $\mathcal{O}$ runs over all hexagonal plaquettes in the lattice, and tunnelling occurs between loops with the opposite sense of flux.

In Ih water ice, in contrast, there are two inequivalent types of six–sided plaquette, illustrated in Fig. 2. The first is composed entirely of centre–symmetric bonds [cf. Fig. 5], and comprises the buckled hexagonal plaquettes which make up the hexagonal–symmetry layers of the Ih structure. A crystal with $N$ oxygen atoms contains $N/2$ such plaquettes, which we label as type I [cf. Fig. 2(a)]. The second is composed of four centre–symmetric and two mirror–symmetric bonds, linking neighbouring layers of the lattice. There are $3N/2$ such plaquettes, which we label as type II [cf. Fig. 2(b)].

Since there are two, inequivalent, types of six-sided plaque in the Ih lattice, the minimal model for quantum effects in Ih water ice comprises two distinct matrix elements

$$\mathcal{H}^{\text{hexagonal}}_{\text{tunnelling}} = -g_1 \sum_{\mathcal{O} \in I} [ | \mathcal{O} \rangle \langle \mathcal{O} | + | \mathcal{O} \rangle \langle \mathcal{O} | ] -g_2 \sum_{\mathcal{O} \in II} [ | \mathcal{O} \rangle \langle \mathcal{O} | + | \mathcal{O} \rangle \langle \mathcal{O} | ] ,$$

acting on the space of all possible proton configurations obeying the ice rules.

Symmetry alone does not place any constraints on the values of $g_1$ and $g_2$, but it is in principle possible to estimate these matrix elements from ab initio calculations. A priori, these matrix elements can take on either sign.
The ab initio studies in Refs. [20–22] conclude that ring tunnelling of the type described by $H_{\text{tunnelling}}$ [Eq. (4)] can be expected to play an important role in hexagonal water ice, but do not give a direct estimate of the size or sign of the matrix elements for this process. Ref. [19] estimates the scale of a single tunnelling matrix element and finds it to be $\sim 1K$. This is consistent with the energy scale of proton dynamics observed in inelastic neutron scattering [18]. We are not aware of any attempt to estimate the two different matrix elements $g_1$ and $g_2$ independently.

Interestingly, a matrix element for tunnelling between ice states of $\sim 1K$ is somewhat larger than the corresponding estimates for the putative “quantum spin ice” materials [33]. Taken at face value, this would suggest that water ice is potentially a more favorable place to look for the formation of an exotic quantum liquid state than are the quantum spin ices.

In Section III of this article, we develop a theory of disordered proton configurations in the presence of quantum tunnelling, based on the minimal quantum model of $Ih$ water ice, $H_{\text{tunnelling}}$ [Eq. (4)]. We make the assumption that

$$g_1 > 0 , \quad g_2 > 0 ,$$

so that the model is accessible to quantum Monte Carlo simulation. Before examining the quantum model, however, it is helpful to revisit the classical proton correlations which arise simply from the ice–rule constraint. This will form the subject of Section III below.

III. PROTON CORRELATIONS IN A CLASSICAL MODEL OF $Ih$ WATER ICE

In what follows, we develop a theory of proton correlations in a classical model of $Ih$ water ice, neglecting all quantum tunnelling between different proton configurations. This theory provides a detailed and microscopically–derivable phenomenology to explain the diffuse scattering which is arises as a result of static proton disorder in $Ih$ water ice [43, 44, 51, 59–65].

We start, in Section III A by developing a long–wavelength, classical field theory of proton configurations in $Ih$ water ice. This field theory has parallels with those developed to explain pinch–points in proton–bonded ferroelectrics [14] and spin–ice [49], but displays a number of new features, which will become important in the quantum case. The details of these calculations are described in Appendix B.

In Section III B, we introduce a lattice theory of proton correlations in classical $Ih$ water ice. This field theory has parallels with those developed to explain pinch–points in proton–bonded ferroelectrics [14] and spin–ice [49], but displays a number of new features, which will become important in the quantum case. The details of these calculations, which are based on a generalisation of a method introduced for spin–ice by Henley [49], are developed in Appendix C.

Then, in Section III C, we use the lattice theory introduced in Section III B to make explicit predictions for the structure factors measured in X–ray [59, 60] and neutron scattering [43, 44, 61] experiments. These show a number of interesting features, which we interpret in terms of the classical
field theory developed in Section III A.

Finally, in Section III D, we compare these predictions with the published literature on $I h$ water ice.

### A. Continuum field–theory for protons in classical $I h$ water ice

The natural place to start in constructing a theory of proton disorder in $I h$ water ice is from the ice rules [11] [2] [6]. The first ice rule state that each bond of the oxygen lattice contains exactly one proton [cf. Section I]. This proton is displaced, relative to the centre of the bond, towards one of the two oxygen atoms which make up the bond [cf. Fig 1]. The displacement of this proton from the centre of the bond $(r'r')$ is thus described using the Ising variable

$$
\sigma_{r'r'} = \pm 1 ,
$$

where $\sigma_{r'r'} = +1$ if the proton is displaced towards $r'$, and $\sigma_{r'r'} = -1$ if it is displaced towards $r$. It follows that

$$
\sigma_{r'r'} = -\sigma_{r' r}.\quad (7)
$$

The second ice rule states that each oxygen must form exactly two short (covalent) and two long (hydrogen) bonds with neighbouring protons. Written in terms of the Ising variable $\sigma_{r'r'}$, this becomes a condition that, at every oxygen lattice site $r$

$$
m_r \equiv \sum_{m_i} \sigma_{r + d_{r_i}} r = 0
$$

where the sum runs over the four nearest—neighbours within the oxygen lattice, located at sites $r + d_{r_i}$. For this purpose, it is necessary to divide the lattice of oxygen sites into four inequivalent sublattices as illustrated in Fig. 4. These four sets of oxygen sites have different associated vectors $d_{r_i}$, defined in Appendix A.

Just as in proton–bonded ferroelectrics [14], or spin ice [49], we can understand the proton correlations arising from Eq. (8) by considering the spatial variation of the flux field represented by the arrows on the bonds in Fig. 2. For each each oxygen–oxygen bond $(rr')$, we assign a flux

$$
P_{rr'} = \frac{r - r'}{a_0} \sigma_{r'r'}
$$

where $a_0$ is the oxygen–oxygen bond distance. This flux points in the direction of the polarisation of the associated H-bond, as illustrated in Fig. 3. The total flux from the four arrows around a single oxygen site is thus

$$
P_r \equiv \sum_{m_i} \frac{1}{a_0} d_{r_i} \sigma_{r + d_{r_i}} r
$$

Knowledge of the fields $m_r$ [Eq. (8)] and $P_r$ [Eq. (10)] on half of the oxygen sites (e.g. those on the A and C sublattices, shown in Fig. 4) is sufficient to uniquely determine the proton configuration of the entire lattice. We can see this as follows: if, for a given oxygen site $r$, we know both $m_r$ (which must be zero for an ice rule state) and $P_r$, we can determine the value of all of the surrounding bond variables $\sigma_{r+d_{r_i}} r$, using the relation

$$
\sigma_{r+d_{r_i}} r = \frac{1}{4} \left( m_r + \frac{3}{a_0} d_{r_i} \cdot P_r \right).
$$

Every bond belongs either to one $A$ oxygen site or one $C$ oxygen site [cf. Fig. 2(b)] so knowing $m_r$ and $P_r$ on just the $A$ and $C$ sites, (or equivalently just the $B$ and $D$ sites) is sufficient.

We may imagine generating a proton configuration by setting $m_r = 0$ on every $A$ and $C$ oxygen site and letting the flux $P_r$ vary between those sites. For the configuration thus obtained to be consistent with the ice rules we would need it to satisfy $m_r = 0$ on all of the $B$ and $D$ tetrahedra as well. Naturally, this implies some constraints on the spatial variation of $P_r$. These constraints control the form of the proton correlations.

The constraints on the spatial variation $P_r$ arising from the ice rules may be understood by defining continuum fields (i.e. defined over all space, not just on the lattice) $P_A(r)$ and $P_C(r)$ in such a way that evaluating them at the lattice sites $r_{A,C}$ returns the value of $P_r$ [Eq. (10)]. If we then assume $P_{A,C}(r)$ to vary smoothly in space, we can use the condition that $m_r$ must vanish at the $B$ and $D$ sites to obtain a constraint on the fields $P_{A,C}(r)$ and their derivatives. This procedure is described in more detail in Appendix B.

Neglecting terms beyond leading order in the bond distance $a_0$, we obtain:

$$
-3\tilde{P}_A(r) + 3\tilde{P}_C(r) - 2a_0 \nabla \cdot P_A
$$

$$
+ 3a_0 \partial_z \tilde{P}_A - 3a_0 \partial_z \tilde{P}_C = 0 \quad (12)
$$

$$
-3\tilde{P}_A(r) + 3\tilde{P}_C(r) - 2a_0 \nabla \cdot P_C
$$

$$
+ 3a_0 \partial_z \tilde{P}_A - 3a_0 \partial_z \tilde{P}_C = 0. \quad (13)
$$

These equations can be decoupled by introducing odd and even combinations of the fields $P_{A,C}(r)$

$$
P_+(r) = \frac{1}{\sqrt{2}} (P_A(r) - \tilde{P}_C(r)) ,
$$

$$
P_-(r) = \frac{1}{\sqrt{2}} (P_A(r) + \tilde{P}_C(r)).
$$

It follows that $P_+(r)$ satisfies a zero–divergence condition

$$
\nabla \cdot P_+(r) = 0 ,
$$

while $P_-(r)$ is governed by the equation

$$
P_-^+(r) + \frac{2}{3} a_0 \nabla \cdot P_-(r) - a_0 \partial_z P_-^+(r) = 0 . \quad (17)
$$

The very different form of the equations governing $P_+$ and $P_-$ suggest that these fields have qualitatively different correlations. Following [25] [49], we can estimate these by assuming a free–energy of the form

$$
F = - (k_B T) \int \frac{d^3 r}{V_{u.c.}} \sum_{\nu = \pm} \frac{\kappa_\nu P_\nu^2}{2}
$$

where $\kappa_\nu$ is an (unknown) constant of entropic origin, and $V_{u.c.}$ is the volume of a unit cell. Within this approximation,
correlations of $P_\pm$ are controlled by a Gaussian distribution of fields

$$p[P_\nu] \propto \exp \left[ -\frac{\kappa_\nu}{2} \int \frac{d^3 r}{V_{u.c.}} P_\nu^2 \right]$$

subject to the constraints Eq. (16) and Eq. (17).

We find that the correlations of $P_+$ have the form of a singular “pinch–point” in reciprocal space

$$\langle P_+^\alpha(-q) P_+^\beta(q) \rangle = \frac{1}{\kappa_+} \left( \delta_{\alpha\beta} \frac{q_\alpha q_\beta}{q^2} \right),$$

$$\langle P_+^\alpha(-q) P_+^\beta(q) \rangle = \frac{1}{\kappa_+} \left( \delta_{\alpha\beta} \frac{q_\alpha q_\beta}{q^2} \right),$$

$$\langle P_+^\alpha(-q) P_+^\beta(q) \rangle = \frac{1}{\kappa_+} \left( 1 - \frac{1}{1 + \frac{q_\alpha^2 q_\beta^2}{4q_\perp^2}} \right),$$

$$\langle P_+^\alpha(-q) P_+^\beta(q) \rangle = \frac{1}{\kappa_+} \left( 1 - \frac{1}{1 + \frac{q_\alpha^2 q_\beta^2}{4q_\perp^2}} \right),$$

where $q_\perp = (q_x, q_y)$

and, for compactness, we have introduced the notation

$$\zeta = \frac{a_0}{3}.$$  \hspace{1cm} (24)

Fourier–transforming Eq. (20)–Eq. (22), we find that correlations of $P_+$ decay algebraically in real space, with the dipolar form

$$\langle P_+^\alpha(r) P_+^\beta(0) \rangle = \frac{4\pi}{\kappa_+} \left[ \delta(r) + \frac{\delta_{\alpha\beta} r^2 - 3r_\alpha r_\beta}{r^5} \right]$$

Meanwhile correlations of $P_-$ are very short–ranged, decaying over a length–scale $\zeta$ [Eq. (24)]. It follows that proton correlations at large distances are controlled by the field $P_+$. The algebraic correlations of $P_+$ give rise to sharp pinch–point singularities in structure factors, of the type observed by Li et al. in neutron scattering from $Ih$ water ice [43]. However in some Brillouin zones, pinch–point singularities are suppressed by the lattice form–factor, and scattering is instead dominated by broad features coming from the correlations of $P_-$. We discuss this point further in Section III C, below, where we develop an explicit theory for neutron and X–ray scattering experiments.

The form of the constraint on $P_+(r)$ [Eq. (16)] strongly suggests an analogy with electromagnetism, where the zero–divergence condition on magnetic field

$$\nabla \cdot B = 0,$$  \hspace{1cm} (26)

can be resolved as

$$B = \nabla \times A,$$ \hspace{1cm} (27)

and the electric and magnetic fields are connected by an underlying $U(1)$ gauge symmetry. This analogy, and the distinction between the two classical fields, $P_+$ and $P_-$, become explicit once quantum effects are taken into account, as described in Section [IV].

B. Lattice theory of proton correlations in classical $Ih$ water ice

The classical fields $P_+$ and $P_-$, introduced in Section [III A], provide a complete description of the correlations of protons in classical $Ih$ water ice at long–wavelength, i.e. near to zone–centers in reciprocal space. However, X–ray and neutron scattering experiments on water ice measure proton correlations at all length–scales. We have therefore developed a lattice–based theory of proton correlations in classical $Ih$ water ice, valid for all wave–numbers. The approach we take is a generalisation of the method developed for spin–ice by Henley [49], in which the ice rules are expressed as a projection operator in reciprocal space. In what follows we explore how the predictions of this theory relate to those obtained from the continuum theory described in Section [III A]. We reserve all technical details for Appendix [C].

The underlying structure of proton correlations in classical $Ih$ water ice is most easily understood throughout the correlations of the Ising variables $\sigma_{\nu\nu'}$ [Eq. (6)], which describe the alternating long and short bonds between protons and neighbouring oxygen atoms. These are characterised by the structure factor

$$S_{Ising}(q) = \sum_{\nu\nu'} \langle \sigma_\nu(q) \sigma_{\nu'}(-q) \rangle,$$ \hspace{1cm} (28)

where the sums on $\nu$ and $\nu'$ run over the eight distinct bonds within the 4–site primitive unit cell, and

$$\sigma_\nu(q) = \sqrt{\frac{4}{N}} \sum_{rr' \in \nu} \exp (-i q \cdot R_{rr'}) \sigma_{rr'},$$

$$R_{rr'} = \frac{r + r'}{2}.$$ \hspace{1cm} (29)

In calculating $\sigma_\nu(q)$, we label the 4 oxygen sublattices within the unit cell A, B, C, D, (cf. Fig [4]), and adopt a sign convention such that

$$r \in \{A, C\}, \ r' \in \{B, D\}.$$ \hspace{1cm} (30)

In Fig [5] we show results for $S_{Ising}(q)$, calculated within the lattice–based theory. The structure factor exhibits clear pinch–point singularities, characteristic of the ice rules [14, 49], at a subset of Brillouin–zone centers typified by

$$Q_p^* = (0, 0, 2),$$ \hspace{1cm} (31)

where, following Nield and Whitworth [44], we index all reciprocal–lattice vectors to the 8–site orthorhombic unit cell defined in Appendix [A].

Correlations near to reciprocal–lattice vectors (Brillouin–zone centres) are described by the classical field theory developed in Section [III A], with contributions from both fields, $P_+$ and $P_-$. Near to a reciprocal lattice vector $Q$, for $|q| \ll 1$, the structure factor can be written

$$S_{Ising}(Q + q) \approx \sum_{\nu = \pm} P_{\nu}^{Ising}(Q) \langle |\lambda_{Q,\nu}^{Ising} \cdot P_{\nu}(q)|^2 \rangle,$$ \hspace{1cm} (32)
where the form–factor $F_{\text{Ising}}(\mathbf{Q})$ [Eq. (D12)] and vectors $\lambda^{\text{Ising}}_{\mathbf{Q},\nu}$ [Eq. (D13)] are defined in Appendix D, and the Fourier transform $P_{\nu}(\mathbf{q})$ [Eq. (C14)] in Appendix C.

Sharp pinch–points are seen for a subset of reciprocal lattice vectors $\mathbf{Q}_p$, for which

$$F_{\text{Ising}}^{-}(\mathbf{Q}_p) = 0.$$  (33)

In this case, correlations are controlled by the zero–divergence condition on $P_{\nu}(\mathbf{q})$ [Eq. (16)], and it follows from Eq. (20) and Eq. (C14) that

$$S_{\text{Ising}}(\mathbf{Q}_p + \mathbf{q}) \approx \frac{F_{\text{Ising}}^{+}(\mathbf{Q}_p)}{\kappa_+} \left( 1 - \frac{\lambda^{\text{Ising}}_{\mathbf{Q},\nu} \cdot \mathbf{q}^2}{|\mathbf{q}|^2} \right).$$  (34)

Considering the specific example of

$$\mathbf{Q}_p^* = (0, 0, 2)$$  (35)

for which

$$\lambda^{\text{Ising}}_{\mathbf{Q}_p^*,+} = (0, 0, 1)$$  (36)

we have

$$S_{\text{Ising}}(\mathbf{Q}_p^* + \mathbf{q}) \propto \left( 1 - \frac{\hat{q}_z^2}{q^2} \right).$$  (37)

This pinch–point, aligned with the hexagonal–symmetry axis ($z$–axis), can be clearly resolved in Fig. 5(b) and (c).

While there are no reciprocal lattice vectors for which $F_{\text{Ising}}^{+}(\mathbf{Q})$ vanishes identically, there are another set of lattice vectors $\mathbf{Q}_m$, for which

$$F_{\text{Ising}}^{+}(\mathbf{Q}_m) \ll F_{\text{Ising}}^{-}(\mathbf{Q}_m)$$  (38)

and the structure factor is dominated by the short–ranged correlations of $P_{\nu}$ [Eq. (17)]. Correlations of this type occurs...
with
\[ Q_m^* = (1, 1, 0) \] (39)
and are visible as a broad feature centred on this reciprocal lattice vector in Fig. 5(a).
For a general reciprocal lattice vector \( Q_{pm} \)
\[ F_{\pm}^{\text{sing}}(Q_{pm}) \sim F_{\pm}^{\text{sing}}(Q_{pm}) \] (40)
and correlations reflect a combination of pinch–points originating in \( P_+(q) \) and broad features originating in \( P_-(q) \). An example of this occurs for
\[ Q_{pm}^* = (2, 0, 0) \] (41)
visible in Fig. 5(a) and (c), where a pinch–point has been superimposed on a featureless background.

Near to zone–centres, where they can be compared, the lattice–based theory is in complete agreement with the predictions of the classical field–theory developed in Section III A. In Appendix C we show how the lattice–based theory reduces to the continuum theory at long–wavelength. We find the that entropic coefficient \( \kappa_+ \), which controls correlations of the fields \( P_v \) [Eq. (20–22)], is independent of \( v \), i.e.
\[ \kappa = \kappa_+ = \kappa_- . \] (42)

To confirm the validity of the lattice–based theory for more general \( q \), we have also performed classical Monte Carlo simulations of Ih water ice, using local loop updates to sample proton configurations within the manifold of states obeying the ice rules. The results, described in Appendix F, are in excellent agreement with the predictions of the lattice theory.

### C. Predictions for scattering from protons in a classical model of Ih water ice

X–ray and neutron scattering experiments on water ice do not measure the structure factor for bond–variables \( S_\text{sing}(q) \) [Eq. (28)], discussed in Section III B, but rather the Fourier transform of the correlation function for the density of protons
\[ S_\text{proton}(q) = \langle n(-q)n(q) \rangle . \] (43)
Information about the proton disorder is contained in the diffuse part of this scattering, which is given by [61]
\[ S_\text{diffuse}_\text{proton}(q) = \sum_{\nu' \nu} \langle \sigma_{\nu'}(-q) \sigma_{\nu}(q) \rangle \sin(q \cdot a_{\nu}) \sin(q \cdot a_{\nu'}) , \] (44)
where \( \sigma_{\nu}(q) \) is given in Eq. (29), and \( a_{\nu} \) is a set of vectors, defined in Appendix A, such that the displacement of a proton from the midpoint on any given bond \( \nu \) is
\[ D_{\nu} = \sigma_{\nu} a_{\nu} , \] (45)
with
\[ |a_{\nu}| \sim 0.15 \ a_0 . \] (46)

In Fig. 6 we show the results for diffuse scattering from protons in a classical model of Ih water ice. The structure factor \( S_\text{diffuse}_\text{proton}(q) \) [Eq. (44)], was calculated using the lattice theory introduced in Section III B. At small momentum transfers, the scattering is suppressed by the factors of \( \sin(q \cdot a_\nu) \) in Eq. (41), and as a result, there is essentially no scattering for \( |q| \gtrsim 2 \). For larger wave number, scattering shows a mixture of broad and sharp features, centered on two different sets of reciprocal lattice vectors. An example of broad feature can be seen near to \( Q = (2, 0, 3) \) in Fig. 6(c). An example of a sharp feature — a pinch–point — can be seen near to \( Q = (4, 0, 0) \) in Fig. 6(a) and (c).

We can relate both broad and sharp features to the correlations of the classical fields \( P_+ \) and \( P_- \), introduced in Section III A. Expanding the structure factor \( S_\text{diffuse}_\text{proton}(q) \) [Eq. (44)] about the reciprocal lattice vector \( Q \), for \( |q| \ll 1 \), we find
\[ S_\text{diffuse}_\text{proton}(Q + q) \approx \sum_{v = \pm} F_{\text{proton}}^v(Q)(\hat{\lambda}^\text{proton}_{Q,v} \cdot P_v(q))^2 , \] (47)
where the form–factors \( F_{\text{proton}}^{\pm}(Q) \) [Eq. (D12)] and vectors \( \hat{\lambda}^\text{proton}_{Q,v} \) [Eq. (D14)] are defined in Appendix D, and the Fourier transform \( F_v(q) \) [Eq. (C14)] in Appendix C.

Once again, there are a subset of reciprocal lattice vectors \( Q_{p,H^+} \) for which
\[ F_{-}^\text{proton}(Q_{p,H^+}) \equiv 0 , \] (48)
and correlations are controlled by the zero–divergence condition on \( P_+ \) [Eq. (16)]. It follows from Eq. (20) and Eq. (14) that
\[ S_\text{diffuse}_\text{proton}(Q_{p,H^+} + q) \approx \frac{F_{+}^\text{proton}(Q_{p,H^+})}{\kappa_+} \left( 1 - \frac{|\hat{\lambda}^\text{proton}_{Q_{p,H^+} + q} |^2}{|q|^2} \right) \] (49)

Considering the specific example of
\[ Q_{p,H^+} = (4, 0, 0) \] (50)
for which
\[ \hat{\lambda}^\text{proton}_{Q_{p,H^+} + q} = (1, 0, 0) , \] (51)
we have
\[ S_\text{diffuse}_\text{proton}(Q_{p,H^+} + q) \propto \left( 1 - \frac{q_x^2}{q_0^2} \right) . \] (52)
A pinch–point singularity of this form is clearly visible near \( Q = (4, 0, 0) \) in Fig. 6(a) and (c).

Similarly, while there are no reciprocal lattice vectors for which \( F_{+}^\text{proton}(Q) \) vanishes identically, there are another set of lattice centers \( Q_{m,H^+} \), for which
\[ F_{+}^\text{proton}(Q_{m,H^+}) \ll F_{-}^\text{proton}(Q_{m,H^+}) \] (53)
The structure factor $S_{\text{diffuse}}(\mathbf{q})$ [Eq. (44)], was calculated using the lattice theory described in Section III C. The Bernal-Fowler “ice-rules” [1] manifest themselves as singular features in scattering (“pinch-points”), clearly visible at, e.g. $\mathbf{Q}_{m,H^+}^* = (0, 0, 4)$ [cf. Refs. [44, 61]]. In addition to this, certain reciprocal-lattice vectors, e.g. $\mathbf{Q}_{m,H^+}^* = (2, 0, 3)$, show broad, asymmetric features. The complete description of both pinch-points and broad features requires the introduction of two distinct classical fields $P_+^*(\mathbf{q})$ and $P_-^*(\mathbf{q})$, as described in Section III A. Reciprocal-lattice vectors are indexed to the orthorhombic unit cell defined in Appendix A, following the conventions of Nield and Whitworth [44].

and scattering from protons reflects the short-ranged correlations of $P_-$ [Eq. (17)]. An example of this type scattering occurs for

$$\mathbf{Q}_{m,H^+}^* = (2, 0, 3).$$

A broad, asymmetric feature, centred on this reciprocal lattice vector, is clearly visible in Fig. 6(c).

For a more general choice of zone centre, $\mathbf{Q}_{pm,H^+}$,

$$F_{\text{proton}}^+(\mathbf{Q}_{pm,H^+}) \approx F_{\text{proton}}^-(\mathbf{Q}_{pm,H^+}),$$

and scattering reflects the correlations of both $P_+$ and $P_-$. An example of this type scattering occurs for

$$\mathbf{Q}_{pm,H^+}^* = (0, 4, 3).$$

A combination of pinch points and broad features can be seen near to this lattice vector in Fig. 6(b).

We conclude this discussion with a brief word of caution — in some cases, the scattering from protons $S_{\text{diffuse}}(\mathbf{q})$ [Eq. (44)] exhibits pinch-points at the same reciprocal lattice vectors as pinch-points in the structure factor $S_{\text{Ising}}(\mathbf{q})$ [Eq. (28)] — as can be seen by comparing Fig. 5 and Fig. 6. However, in general

$$F_{\text{proton}}^+(\mathbf{Q}) = 0 \not\Rightarrow F_{\text{Ising}}^-(\mathbf{Q}) = 0,$$

and pinch-points in $S_{\text{diffuse}}(\mathbf{q})$ do not, necessarily, occur at the same reciprocal lattice vectors as pinch-points in $S_{\text{Ising}}(\mathbf{q})$.

D. Comparison with published results for Ih water ice

That the ice rules give rise to pinch point singularities in the structure factor is a very general result and widely known from the study of ice-like systems [14, 25, 49], with the prediction that the proton correlation function should be singular at Brillouin zone centres going back as far as Villain in 1972.
These singularities are also visible in Monte Carlo simulations of the structure factor, based on the ice rules [60] and in reverse Monte Carlo fits to neutron scattering data [43,44,62,63].

Other theoretical studies, which have utilised random walk approximations [61,64] and graph series expansions [65], while not specifically identifying the pinch points, have noted the presence of nodal lines in the structure factor. These are also predicted by our lattice theory [Fig. 5].

Experimental observation of these pinch points in water ice is rendered more difficult since the pinch points are located at reciprocal lattice vectors. This means that they occur beneath the Bragg peaks of the crystal structure. Nevertheless, these structures are visible in the neutron scattering data obtained from deuterated water ice (D2O) [44]. The nodal lines can also been seen in this data as marked suppressions of the scattering along certain high symmetry directions of reciprocal space. At other reciprocal lattice vectors (e.g. \( \mathbf{Q}_m = (2,0,3) \)) the experimental scattering is rather broad [43], as predicted here.

Where our theory predicts a substantial contribution to the structure factor from correlations of both \( \mathbf{P}_+ \) and \( \mathbf{P}_- \) (e.g. at \( \mathbf{Q}_m = (2,0,3) \)) it is difficult to distinguish a sharp pinch point (due to \( \mathbf{P}_+ \)) against the broad background (due to \( \mathbf{P}_- \)) in the experimental data [44]. This may be difficult in general with finite experimental resolution and the pinch points are best observed around reciprocal lattice vectors where the contribution to the structure factor from \( \mathbf{P}_- \) is vanishing or very small, such as \( \mathbf{Q}_m = (2,0,0) \).

There have also been X-ray diffraction measurements of the diffuse scattering from \( \text{IH} \) water ice [59,60]. The recent analysis of Wehinger et al. [60] concludes that the X-ray diffraction is dominated by thermally excited phonons making the contribution from the static hydrogen disorder difficult to isolate. This difficulty may be alleviated at sufficiently low temperature where the density of thermally excited phonons is suppressed.

Pinch–point singularities, analogous to those found in water ice, were first observed in proton bonded ferroelectrics [14], and have now been reported in a number of frustrated magnets, including Ho2Ti2O7 [66], Tb2Ti2O7 [67], Yb2Ti2O7 [68] and Pr2Zr2O7 [69], where they indicate an algebraic correlation of spins. The pinch point singularities in the cubic “spin ice” Ho2Ti2O7 [66], in particular, have been widely discussed, and are now very well understood [25,49,70,71].

In the spin ice case, these singularities can be thought of as arising from a zero divergence condition on an effective magnetic field \( \mathbf{B} \), derived from the magnetization of a single tetrahedron within the pyrochlore lattice. This effective magnetic field plays the same role in spin ice as the uniform polarisation \( \mathbf{P}_+ \) [Eq. (14)] in hexagonal water ice. However, in spin ice, where the primitive unit cell comprises a single tetrahedron, there is no analogue of the staggered field \( \mathbf{P}_- \) [Eq. (15)], introduced in Section III A.

At long wavelengths, the correlations of \( \mathbf{B} \) in a spin ice take precisely the same form as the correlations of \( \mathbf{P}_+ \) [Eq. (20)] in \( \text{IH} \) water ice. The relationship between the correlations of these divergenceless fields and the structure factor which is measured in scattering experiments — given by Eq. (47) for the case of ice \( \text{IH} \) — is, however, different. This changes both the selection rules defining at which Brillouin zone centers pinch points will be visible, and the orientation of the pinch points with respect to the reciprocal lattice vector \( \mathbf{Q} \).

**IV. PROTON TUNNELLING AND EMERGENT PHOTONS IN A QUANTUM MODEL OF \( \text{IH} \) WATER ICE**

The analogy between the ice–rules and electromagnetism, underpinning the classical analysis of Section III, becomes complete once quantum effects are taken into account. In what follows, we show that the minimal model for quantum effects in \( \text{IH} \) water ice, \( \mathcal{H}_\text{hexagonal} \) tunnelling [Eq. (4)], leads to a compact, frustrated quantum U(1) lattice–gauge theory, with precisely the form of electromagnetism on a lattice. We explore the new features of a proton liquid described by such a theory, and make explicit predictions for both inelastic and quasi–elastic (energy–integrated) scattering of X–rays or neutrons from disordered protons in a quantum \( \text{IH} \) water ice. This discussion proceeds as follows:

Firstly, in Section IV A we outline the derivation of this lattice–gauge theory. Technical details of these calculations are provided in Appendix E.

Then, in Section IV B we explore some of the features of lattice gauge theory in its deconfined (proton–disordered) phase. In particular, we show how its low–energy excitations can be thought of as the linearly—dispersing, birefringent “photons”, and how these relate to the classical fields \( \mathbf{P}_+ \) and \( \mathbf{P}_- \) introduced in Section III.

Finally, in Section IV C we discuss the experimental signatures of a quantum water ice, described by the deconfined phase of the lattice gauge theory.

### A. Lattice–gauge theory

Our route to a lattice–gauge theory of \( \text{IH} \) water ice closely parallels the cubic–symmetry case previously considered by Hermle et al. [31], and Benton et al. [33].

The theory itself, however, contains a number of new features. We begin introducing a set of pseudospin–1/2 operators \( S^z, S^+, S^- \) defined on the bonds \( \mathbf{r} \mathbf{r}' \) of the oxygen lattice. The z–component of the pseudo-spin is directly proportional to the Ising variable \( \sigma_{\mathbf{r} \mathbf{r}'} \) [Eq. (3)], introduced to describe proton–correlations in the classical case

\[
S^z_{\mathbf{r} \mathbf{r}'} = \frac{1}{2} \sigma_{\mathbf{r} \mathbf{r}'} = -S^z_{\mathbf{r}' \mathbf{r}}. 
\]

In keeping with the directedness of \( S^z_{\mathbf{r} \mathbf{r}'} \) [Eq. (58)] the ladder operators obey the identity

\[
S^+_{\mathbf{r} \mathbf{r}'} = S^-_{\mathbf{r}' \mathbf{r}}. 
\]

The minimal quantum model for \( \text{IH} \) water ice \( \mathcal{H}_\text{hexagonal} \) tunnelling [Eq. (4)], can be expressed in terms of these
operators as
\[
\mathcal{H}_{\text{tunnelling}}^{\text{hexagonal}} = -g_1 \sum_{\mathcal{O} \in I} \left[ S_1^+ S_2^- S_3^+ S_4^- S_5^+ S_6^- + \text{h.c.} \right] - g_2 \sum_{\mathcal{O} \in \mathcal{I}} \left[ S_1^+ S_2^- S_3^+ S_4^- S_5^+ S_6^- + \text{h.c.} \right]. \tag{60}
\]

A mapping to a \(U(1)\) lattice–gauge theory is then possible by writing the spin-1/2 operators in a quantum rotor representation \([31, 41, 72]\)
\[
S^z_{rr'} \rightarrow E_{rr'} \quad S^\pm_{rr'} \rightarrow e^{\pm iA_{rr'}}, \tag{61}
\]
subject to the canonical commutation relation
\[
[E_{rr'}, A_{rr''}] = i\delta_{rr'} \delta_{rr''}. \tag{62}
\]
The commutation relation Eq. (62) is familiar in quantum electromagnetism as the commutation between an electric field \(E\) and a vector potential \(A\), and substituting the rotor representation Eq. (61) into Eq. (60) results in a compact \(U(1)\) gauge theory
\[
\mathcal{H}_{\text{U(1)}}^{\text{compact}} = -2g_1 \sum_{\mathcal{O} \in I} \cos\left(\nabla \times A\right) - 2g_2 \sum_{\mathcal{O} \in \mathcal{I}} \cos\left(\nabla \times A\right). \tag{63}
\]
where the sum \(\sum_{(rr') \in \mathcal{S}}\) runs over centre–symmetric oxygen–oxygen bonds, \(\sum_{(rr') \in \mathcal{MS}}\) runs over mirror–symmetric bonds [cf. Fig. 3] and \(\nabla \times A\) represents the lattice curl of \(A_{rr'}\) around a hexagonal plaquette, which may be of type–I or type–II [cf. Fig. 2].

The electric field \(E_{rr'}\) subject to the constraint that
\[
E_{rr'} = \pm \frac{1}{2} \quad \forall \text{ bonds } rr'. \tag{64}
\]
Following \([31, 33]\), one may then argue that averaging over fast fluctuations of the gauge field softens the constraint Eq. (64), and leads to a non–compact gauge theory on the links of the \(I\)th water ice lattice
\[
\mathcal{H}_{\text{U(1)}} = \frac{\mathcal{U}}{2} \sum_{(rr') \in \mathcal{S}} E_{rr'}^2 + \frac{\mathcal{U}'}{2} \sum_{(rr') \in \mathcal{MS}} E_{rr'}^2 + \frac{\mathcal{K}}{2} \sum_{\mathcal{O} \in I} \left[\nabla \times A\right]^2 + \frac{\mathcal{K}'}{2} \sum_{\mathcal{O} \in \mathcal{I}} \left[\nabla \times A\right]^2 \tag{65}
\]
The parameters \(\mathcal{U}\) and \(\mathcal{U}'\) may be thought of as Lagrange multipliers fixing the average value of \(E_{rr'}^2\) on the two inequivalent types of bond. The average over fast fluctuations will in general renormalise \(\mathcal{K}\) and \(\mathcal{K}'\) from their “bare” values
\[
K_0 = 2g_1 \quad K'_0 = 2g_2. \tag{66}
\]
The phase diagram of the lattice–gauge theory \(\mathcal{H}_{\text{U(1)}}\) [Eq. (65)] will possess both a deconfined phase, in which the protons form a disordered quantum fluid, and confined phase(s), in which the protons order. In what follows we confine our discussion to the deconfined phase of \(\mathcal{H}_{\text{U(1)}}\), without attempting to characterise competing fixed points.

Even within this deconfined phase, the validity of \(\mathcal{H}_{\text{U(1)}}\) [Eq. (65)] depends critically on the assumptions made in passing to a non–compact gauge theory. While these assumptions are reasonable, they can ultimately only be validated through quantum Monte Carlo simulation of the microscopic model \(\mathcal{H}_{\text{tunnelling}}^{\text{hexagonal}}\) [Eq. (60)] — cf. \([33, 35, 39, 40]\).

We have therefore used variational quantum Monte Carlo (VMC) simulation of \(\mathcal{H}_{\text{U(1)}}\) to establish that the deconfined phase of the lattice gauge theory, \(\mathcal{H}_{\text{U(1)}}\) [Eq. (65)], closely describes the correlations of the microscopic model \(\mathcal{H}_{\text{tunnelling}}^{\text{hexagonal}}\) [Eq. (60)], for the symmetric choice of parameters \(g_1 = g_2\). These results are presented in Appendix E. In principle, it is also possible to extract the parameters of the lattice gauge theory — \(\mathcal{U}, \mathcal{U}', \mathcal{K}\) and \(\mathcal{K}'\) — from detailed Quantum Monte Carlo simulation of the microscopic model \(\mathcal{H}_{\text{tunnelling}}^{\text{hexagonal}}\) as a function of \(g_1\) and \(g_2\) — cf. Refs. [33]. However since the purpose of this Article is to explore the properties of the deconfined phase, and no reliable estimates are yet available for \(g_1\) and \(g_2\), we treat \(\mathcal{U}, \mathcal{U}', \mathcal{K}\) and \(\mathcal{K}'\) as phenomenological parameters.

B. Phenomenology of the deconfined phase : Why these photons?

In the absence of charges, the defining characteristic of the deconfined phase of the \(U(1)\) lattice gauge theory, \(\mathcal{H}_{\text{U(1)}}\) [Eq. (65)], is its “photon”, a transverse excitation of the gauge field \(A\), with definite polarization and linear dispersion at long wavelength. Since \(\mathcal{H}_{\text{U(1)}}\) is quadratic in \(A\), it can be solved by introducing a suitable basis for transverse fluctuations of the gauge–field. This calculation is explained in detail in Appendix E following the methods described in Ref. [33]. Here we concentrate instead on using this solution of \(\mathcal{H}_{\text{U(1)}}\) to describe the new features which arise from the tunnelling of protons in water ice.

In Fig. 7, we show the dispersion of the excitations of \(\mathcal{H}_{\text{U(1)}}\) [Eq. (65)], for the symmetric choice of parameters
\[
\mathcal{U} = \mathcal{U}', \quad \mathcal{K} = \mathcal{K}'. \tag{67}
\]
The dispersion is normalised to the characteristic energy–scale of the lattice–gauge theory, \(\sqrt{\mathcal{U}\mathcal{K}}\), and has an overall bandwidth
\[
\Delta \omega = f \left(\frac{\mathcal{U}'}{\mathcal{U}}\right) \sqrt{\mathcal{U}\mathcal{K}}, \tag{68}
\]
where, for this parameter set
\[
f(1, 1) \approx 4.56. \tag{69}
\]

On the basis of published simulations for quantum spinice \([32, 34]\), it is reasonable to expect that the bandwidth of the excitations of the gauge theory, \(\Delta \omega\), is of the same magnitude as the quantum tunnelling \(g\).

The dispersion shown in Fig. 7 possesses at least two remarkable features, which mark the present case out as different from the cubic symmetry case discussed in Ref. [33]. Firstly, in addition to the gapless, linearly dispersing, modes
at low energy there are two gapped modes. Secondly, for wavevectors which are not parallel to the crystallographic z-axis, the two linearly dispersing modes are non-degenerate. This is an example of the phenomenon of birefringence, in which the dispersion relation of a photon depends on its polarisation, in this case applied to emergent photons. This mirrors the fact that birefringence is also observed in the propagation of real photons through crystals of Ih water ice [73, 74].

Both of these results- the presence of the gapped modes and the birefringence of the gapless modes are readily understandable in the light of the classical analysis presented in Section III. The constraints on the fields $P_+$ and $P_-$ [Eqs. (16)-(17)] commute with $H_{\text{hexagonal}}^{\text{tunneling}}$ and are therefore preserved in the presence of quantum tunneling. The quantum fluctuations of these fields must therefore respect Eqs. (16)-(17).

In the case of $P_+$ this is ensured by writing

$$P_+ = \nabla \times A'$$

where we note that $A' \neq A_{\text{eff}}$, which appears in Eq. (65).

The form of the Lagrangian describing fluctuations of $A'$ is then the Maxwell Lagrangian, modified according to the hexagonal symmetry of the lattice. Choosing the Coulomb gauge

$$\nabla \cdot A' = 0$$

the Lagrangian is

$$\mathcal{L}_{\text{hex}}^{\text{Maxwell}} = \frac{1}{2} \int dt \int d^3r \sum_{\alpha, \beta}$$

$$\left[ \rho_{\alpha\beta} \partial_t A'^{\alpha} \partial_\gamma A'^{\beta} - \nu_{\alpha\beta} (\nabla \times A')^{\alpha} (\nabla \times A')^{\beta} \right].$$

The tensors $\rho$ and $\nu$ are diagonal in the crystal basis and have
FIG. 8. (Color online). Prediction for quasi-elastic scattering from protons in a quantum model of Ih water ice at zero temperature \((T = 0)\). The “pinch–points” associated with the ice–rules [cf. Fig. 6], are eliminated by quantum fluctuations [cf. Ref. [35]]. At finite temperatures, these pinch–points will be restored with a weight linear in \(T\) [33]. Results are shown for the energy–integrated, equal–time structure factor \(S_{H+}(q, t = 0)\) [Eq. 78], calculated within the lattice–gauge theory \(H_{U(1)}\) [Eq. (65)], for the same parameter set [Eq. (67)] as Fig. 7. Reciprocal–lattice vectors are indexed to the orthorhombic unit cell defined in Appendix [A] following the conventions of Nield and Whitworth [44].

The photons, which are the excitations of Eq. (71) are then degenerate when propagating with momentum parallel to the crystallographic z-axis, having a dispersion relation

\[
\omega = \sqrt{\frac{\nu_\perp}{\rho_\perp}} |k|. \tag{74}
\]

When propagating in the plane perpendicular to the crystallographic z-axis the two photon modes are non-degenerate having dispersion relations

\[
\omega_1 = \sqrt{\frac{\nu_\perp}{\rho_z}} |k|, \quad \omega_2 = \sqrt{\frac{\nu_\perp}{\rho_\perp}} |k|. \tag{75}
\]

The field, \(P_\perp\), which has exponentially decaying correlations in the classical problem has no associated gauge symmetry. Due to the constraint Eq. (17), it’s fluctuations may be entirely described by a Lagrangian in terms of it’s planar components \(P_\perp\), with the z-component being fixed by Eq. (17). The Lagrangian describing the fluctuations of \(P_\perp\) has the form

\[
\mathcal{L}_- = \frac{1}{2} \int dt \int d^3r \left[ \gamma (\partial_\perp P_\perp)^2 - \Delta (P_\perp)^2 \right] - \sum_{\alpha\beta=x,y,z} \epsilon_{\alpha\beta} \partial_\alpha P_\perp^\alpha \partial_\beta P_\perp^\beta \tag{76}
\]

The form of the tensor \(\epsilon\) is dictated by the symmetry of the lattice. The excitations of \(P_\perp\) are gapped modes which become degenerate approaching \(q = 0\), with a gap at zero momentum

\[
\omega(q = 0) = \sqrt{\frac{\Delta}{\gamma}}. \tag{77}
\]
In the limit \( q \to 0 \) we therefore identify the gapped modes as being associated with quantised fluctuations of \( P^- \) and the gapless modes as being associated with quantised fluctuations of \( P^+ \). This is demonstrated explicitly in Appendix E.

### C. Predictions for coherent neutron experiments

The formation of the quantum liquid state at \( T = 0 \) would have profound consequences for scattering experiments. In this section we will briefly comment on what one could expect to observe in a measurement of the coherent scattering from water ice, in the scenario where quantum tunnelling of protons leads to the formation of a fluctuating \( U(1) \) liquid state. We shall postpone a discussion of the consequences for measurements of incoherent scattering, such as that performed by Bove et al in [18] until Section V.

Fig. 8 shows the equal time (energy-integrated) structure factor for the diffuse coherent scattering from disordered protons at \( T = 0 \)

\[
S_{\text{diffuse}}(\mathbf{q}, t = 0) = 4 \sum_{ij} \sin(q \cdot a_i) \sin(q \cdot a_j)
\]

The pinch points are absent at \( T = 0 \), replaced by suppressions of the scattering around Brillion zone centers [33, 33, 72].

This effect is most clearly understood by comparing Fig. 8 with the corresponding classical result shown in Fig. 6 around certain reciprocal lattice vectors, e.g.

\[
Q_p = (2, 0, 0)
\]

the classical scattering is directly proportional to a correlation function of \( P^- \) with no contribution from the short range correlated field \( P^+ \) and takes the form given in Eq. (52), i.e.

\[
S_{\text{proton}}^\text{diffuse}(Q_p + q) \propto \left( 1 - \frac{q \cdot Q_p}{q^2 Q_p^2} \right)
\]

In the quantum case the pinch point form of Eq. (52) becomes modified by a factor of \( q \), suppressing the pinch point

\[
S_{\text{diffuse}}(Q_p + q, t = 0) \propto q \left( 1 - \frac{q \cdot Q_p^2}{q^2 Q_p^2} \right).
\]

At finite temperature these pinch points are restored with a weight linear in \( T \) [33]. This being the case, the clearest signature of the formation of a quantum liquid which could be obtained from energy integrated scattering is the observation of a pinch point at high temperature, the intensity of which reduces in as the system cooled, heading towards a linear suppression of the scattering of the form of Eq. (80) as \( T \to 0 \).

The nodal lines which are predicted in the classical scattering [Fig. 5] remain nodal in the quantum case [Fig. 5].

Around other reciprocal lattice vectors e.g

\[
Q_m = (2, 0, 3)
\]

there is a large contribution to the scattering from the fluctuations of \( P^- \). In these cases the broad features present in the classical scattering remain present in the quantum case at \( T = 0 \), but are now shifted to finite energy in accordance with the gapped nature of the fluctuations of \( P^- \).

Around reciprocal lattice vectors such as

\[
Q_m = (0, 4, 3)
\]

where the classical scattering shows a combination of pinch points and broad features, the quantum theory predicts that the pinch point contribution will be linearly suppressed \( T = 0 \), as in Eq. (80), while the broad feature will remain, albeit shifted to a finite energy.

This separation of the fluctuations of \( P^+ \) and \( P^- \) as a function of energy would be clearly manifested in a measurement of the inelastic scattering. This is illustrated in Fig. 7 which shows a prediction for the inelastic scattering around the reciprocal lattice vector \( \mathbf{Q}_m = (0, 2, 4) \) at \( T = 0 \).

The linearly dispersing photon modes are visible with intensity \( \propto q \propto \omega \), vanishing as they approach \( \omega = 0 \) at the zone center. The gapped modes have finite weight approaching the zone center. Observation of these modes in an inelastic scattering experiment would represent convincing evidence for the formation of protonic quantum liquid in ice \( \text{Ih} \).

### V. DISCUSSION AND CONCLUSIONS

In this article we have derived a theory of the proton disorder in \( \text{Ih} \) water ice which incorporates quantum tunnelling between different proton configurations obeying the Bernal-Fowler “ice-rules” [1, 2]. Starting from a microscopic model of tunnelling on the hexagonal plaquettes of the \( \text{Ih} \) lattice, \( \mathcal{H}^{\text{tunneling}} \) [Eq. (8)], we have obtained a description of the resulting quantum proton liquid in terms of a \( U(1) \) gauge theory \( \mathcal{H}^{\text{gauge}} \) [Eq. (3)], [Section IV]. We have also constructed an equivalent theory of proton correlations in a classical model of \( \text{Ih} \) water ice [Section III], which describes the proton correlations at temperatures greater than the energy scale of the quantum tunnelling \( T \geq g_1, g_2 \).

Both quantum and classical theories contain a number of interesting new features, not seen in equivalent treatments of spin ice [31, 33, 49]. In particular, the lattice gauge theory now supports transverse fluctuations of both a divergenceless, algebraically correlated field \( P^+ \), which have the character of emergent photons, and gapped fluctuations of an exponentially correlated field \( P^- \). Just like real photons in \( \text{Ih} \) water ice, these emergent photons are birefringent, exhibiting dispersion which depends on both their polarisation and their direction of propagation [Fig. 7, Section V].

We have also used the lattice gauge theory to make explicit predictions for inelastic scattering of neutrons or X-rays from the protons in \( \text{Ih} \) water ice. We find that the “pinch-points”, characteristic of scattering from systems obeying the “ice rules” [Fig. 6], are eliminated by quantum fluctuations at \( T = 0 \) [Fig. 8].

Perhaps the strongest evidence in support of proton–tunnelling of the type considered in this article comes from
(a) Symmetric parameter set, as defined in Eq. (83).

(b) Asymmetric parameter set, as defined in Eq. (84).

FIG. 9. (Color online). Prediction for inelastic, incoherent scattering from protons in quantum Ih water ice. Inelastic scattering from the excitations of the proton liquid appears as “wings” (shaded yellow) which can be seen above the tails of the elastic line (shaded purple), as observed by Bove et al. [18]. (a) Prediction of lattice gauge theory \( H_{(1)} \) [Eq. (65)], at a temperature \( T = 5 \) K, for the parameter set [Eq. (83)], equivalent to that used when discussing coherent inelastic scattering [cf. Fig. 7 and Fig. 8]. (b) Results for a parameter set with a more anisotropic photon dispersion, as defined in Eq. (84). In both cases, the overall photon energy scale was set such that the bandwidth is \( \Delta \omega \sim 0.1 \) meV. Results for the incoherent inelastic structure factor \( S_{inc}(q, \omega) \) [Eq. (81)], were integrated over angle, and convoluted with a sum of two Gaussians representing the experimental resolution of Ref. [18], as described in Appendix G.

Given this coincidence of energy scales, it is interesting to compare the predictions of the theory of a quantum water ice developed in this article, with the neutron-scattering experiments of Bove et al. [18]. In these experiments, inelastic, incoherent scattering from protons in Ih water ice at \( T = 5 \) K, was observed for a range of energies \( \Delta \omega \sim 0.1 \) meV, outside the experimental width of the elastic line. The authors found that the momentum dependence of this incoherent signal was consistent with a “double well” model in which there is one proton on each bond, tunnelling between two sites. Since moving a single proton within a state obeying the ice rules has a prohibitive energy cost, they interpreted their result in terms of correlated tunnelling of protons on hexagonal placates [cf. Fig. 2]. This suggestion, and the energy-scale of the dynamics observed, find support in \textit{ab initio} calculations for Ih water ice [19][21], which find quantum tunnelling \( g \sim 0.1 \) meV [19].

Recent neutron scattering experiments by Bove et al. [18]. In these experiments, inelastic, incoherent scattering from protons in Ih water ice at \( T = 5 \) K, was observed for a range of energies \( \Delta \omega \sim 0.1 \) meV, outside the experimental width of the elastic line. The authors found that the momentum dependence of this incoherent signal was consistent with a “double well” model in which there is one proton on each bond, tunnelling between two sites. Since moving a single proton within a state obeying the ice rules has a prohibitive energy cost, they interpreted their result in terms of correlated tunnelling of protons on hexagonal placates [cf. Fig. 2]. This suggestion, and the energy-scale of the dynamics observed, find support in \textit{ab initio} calculations for Ih water ice [19][21], which find quantum tunnelling \( g \sim 0.1 \) meV [19].

Since incoherent scattering probes only the local proton correlations, it is not capable of distinguishing the signal long-wavelength features of the lattice-gauge theory, such as birefringent photons, or temperature–dependent pinch–points. Nonetheless, comparison of the these predictions with experiment remains very intriguing. We find that the quantum tunnelling of protons does indeed produce “wings” of inelastic scattering which extend appreciably beyond the experimental width of the elastic line, as observed by Bove et al. [18]. The high–energy “tails” of this scattering are not as extended as those found in experiment, and for the symmetric choice of parameters [Fig. 9(a)], the excitations of the lattice-gauge theory also show more structure at intermediate energies than is seen in experiment. However, better agreement is found for the assymetric choice of parameters [Fig. 9(b)], and phonons, neglected, in our theory, may also contribute to the high–energy part of the tail.

\[
\frac{\mathcal{K}'}{\mathcal{K}} = 1.0, \quad \frac{\mathcal{U}'}{\mathcal{U}} = 1.0, \quad \sqrt{\frac{\mathcal{U}}{\mathcal{K}}} = 5.4, \quad \sqrt{\frac{\mathcal{U}}{\mathcal{K}}} = 0.018 \text{ meV},
\]  

\[
\mathcal{U} = 5.4, \quad \mathcal{K} = 0.018 \text{ meV},
\]  

\[
\mathcal{K'} \mathcal{K} = 3.0, \quad \mathcal{U'} \mathcal{U} = 2.05, \quad \sqrt{\frac{\mathcal{U}}{\mathcal{K}}} = 4.83, \quad \mathcal{U} = 0.012 \text{ meV}.
\]  

Both parameter sets give an overall bandwidth of excitations [Eq. (68)]

\[
\Delta \omega \sim 0.1 \text{ meV} \sim 1 \text{ K},
\]  

consistent with \textit{ab initio} estimates of \( g \) [19]. The details of the calculation are explained in Appendix G.

\[
\frac{\mathcal{K}'}{\mathcal{K}} = 1.0, \quad \frac{\mathcal{U}'}{\mathcal{U}} = 1.0, \quad \sqrt{\frac{\mathcal{U}}{\mathcal{K}}} = 5.4, \quad \sqrt{\frac{\mathcal{U}}{\mathcal{K}}} = 0.018 \text{ meV},
\]  

\[
\mathcal{U} = 5.4, \quad \mathcal{K} = 0.018 \text{ meV},
\]  

\[
\mathcal{K'} \mathcal{K} = 3.0, \quad \mathcal{U'} \mathcal{U} = 2.05, \quad \sqrt{\frac{\mathcal{U}}{\mathcal{K}}} = 4.83, \quad \mathcal{U} = 0.012 \text{ meV}.
\]  

\[
\Delta \omega \sim 0.1 \text{ meV} \sim 1 \text{ K},
\]  

consistent with \textit{ab initio} estimates of \( g \) [19]. The details of the calculation are explained in Appendix G.
While this agreement is very encouraging, it is hard to draw a definitive conclusion on the nature of Ih water ice from incoherent scattering alone. A much cleaner test would be a measurement of the dispersion of the emergent photons, and associated gapped modes, as a function of wave vector. This would require coherent inelastic scattering, which is rendered rather challenging by the fact that incoherent neutron scattering cross section for protons is $\sim 50$ times greater than the coherent cross section \cite{75}. However, in some circumstances, it is possible to separate coherent and incoherent scattering using polarisation analysis \cite{76}.

To enhance the ratio of coherent to incoherent scattering one could use deuterated ice, D$_2$O \cite{43}. However, some caution is called for here. There is evidence that partial deuteration inhibits the quantum tunnelling by localising ionic defects, preventing their virtual passage around a loop \cite{18,22}. It may be that the dynamics is restored in the case of full (or very large) deuteration, but even so the change from protons to deuterons may alter the relevant temperature scale to observe the quantum liquid, or cause the system to freeze or order.

A possible alternative to neutron scattering is X-ray diffraction. In this it has been shown that at high temperatures the diffuse scattering is dominated by thermally excited phonons \cite{60}, making it difficult to observe the diffuse scattering which comes from the proton disorder. However, the quantum effects described in this article should manifest themselves at temperatures far below the phonon Debye temperature. At these temperatures the contribution of thermally excited phonons should be substantially reduced and one may hope to observe the correlations associated with the onset of a quantum proton liquid regime.

It is also interesting to speculate that the optical properties of Ih water ice, which so closely resemble those of the emergent photons in the lattice gauge theory, might be sensitive to a proton-liquid at low temperatures. A quantum liquid of protons could also manifest itself in a $T^0$ contribution to the heat-capacity of Ih water ice at low temperatures, coming from thermal excitation of the emergent photons \cite{33,35}.

Such experiments could also be of interest in other water ices, where protons order at low temperatures. The assertion, in Ref. \cite{41}, that the lattice gauge theory should be confining at $T = 0$ in 2D, is consistent with numerical results for quantum ice in 2D \cite{15,77,79}. However a number three-dimensional ice-like models are known to support deconfined, quantum-liquid ground states \cite{35,39}, and results in this article suggest that a quantum-liquid ground states remains a possibility for Ih water ice. And even if protons do order at $T = 0$, experience with other ice models suggests that a quantum liquid may still be observable at finite temperature \cite{32,14,79}.

In conclusion, more than 80 years after the pioneering work of Bernal and Fowler, the behaviour of protons in water ice at low temperatures remains a problem of great fundamental interest. The possibility of a quantum liquid of protons in Ih water ice, of the type explored in this Article, remains a tantalising possibility. And experimental evidence for quantum tunnelling between different proton configurations, found in inelastic neutron scattering \cite{18}, suggest that this possibility merits further investigation.

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Since completing this work, we have become aware of a recent preprint by Isakov et al., which also examines the proton correlations in a classical model of Ih water ice.

**Appendix A: Details of the lattice and coordinate system**

In this Appendix we give details of the lattice and coordinate system which we have used in our calculations. We will write all lattice length scales in terms of the oxygen-oxygen bond distance, $a_0$, which in Ih water ice is approximately $10$

$$a_0 \approx 2.75 \text{ Å}. \quad (A1)$$

We use a coordinate system in which the hexagonal symmetry axis is the $z$-axis and the repeat vectors of the hexagonal unit cell

$$G_1 = a_0 \left( \frac{2\sqrt{2}}{\sqrt{3}}, 0, 0 \right) \quad (A2)$$

$$G_2 = a_0 \left( \frac{\sqrt{2}}{\sqrt{3}}, \sqrt{2}, 0 \right) \quad (A3)$$

$$G_3 = a_0 \left( 0, 0, \frac{8}{3} \right). \quad (A4)$$

The primitive unit cell contains four oxygen atoms and eight protons.

One can also define an orthorhombic unit cell, containing eight oxygen atoms with orthogonal repeat vectors

$$G_{X} = G_1 \quad (A5)$$

$$G_{Y} = 2G_2 - G_1 \quad (A6)$$

$$G_{Z} = G_3. \quad (A7)$$

This is the unit cell used by Nield and Whitworth in Ref. \cite{44}.

In the scattering patterns shown in Figs. 5, 6, 13 and 8 the reciprocal lattice units used for the momentum scale are with reference to the orthorhombic unit cell, as in Ref. \cite{44}. Thus, $h$, $k$ and $l$ [cf. Figs. 5, 6, 13 and 8] relate to the momentum transfer $q$ via

$$q = \frac{2\pi h}{|G_X|}, \frac{2\pi k}{|G_Y|}, \frac{2\pi l}{|G_Z|}. \quad (A8)$$

where $G_{XYZ}$ are defined in Eqs. (A5)-(A7).
FIG. 10. (Color online). Labelling convention for the eight sets of oxygen–oxygen bonds and eight sets of six-link plaquettes unrelated by translational symmetry. This is the convention employed in diagonalising the lattice gauge theory described in Section IV and Appendix E. (a) is color-coded such that bonds related by translational symmetry are the same color. The bonds labelled 0 and 4 are mirror symmetric bonds aligned along the z-axis and the remaining bonds are center symmetric [cf. Fig. 3]. (b) shows plaquettes of type I with matrix element $g_1$. (c)-(e) shows plaquettes of type II with matrix element $g_2$.

The bond vectors $d_{i}^{\alpha}$ connecting an oxygen to its four neighbours [cf. Eq. (8)] are given by

\begin{align*}
\mathbf{d}_0^A &= a_O (0, 0, 1) & \text{(A9)}
\mathbf{d}_1^A &= a_O \left( \frac{\sqrt{2}}{3}, \frac{\sqrt{2}}{3}, -\frac{1}{3} \right) & \text{(A10)}
\mathbf{d}_2^A &= a_O \left( -\frac{\sqrt{2}}{3}, \frac{\sqrt{2}}{3}, -\frac{1}{3} \right) & \text{(A11)}
\mathbf{d}_3^A &= a_O \left( 0, -\frac{2\sqrt{2}}{3}, -\frac{1}{3} \right) & \text{(A12)}
\mathbf{d}_1^C &= a_O \left( -\frac{\sqrt{2}}{3}, -\frac{\sqrt{2}}{3}, -\frac{1}{3} \right) & \text{(A13)}
\end{align*}
\[ d_i^C = a_0 \left( \sqrt{\frac{2}{3}} - \frac{2}{3}, -\frac{1}{3} \right) \quad (A14) \]
\[ d_i^A = a_0 \left( 0, \frac{2\sqrt{2}}{3}, -\frac{1}{3} \right) \quad (A15) \]
\[ d_i^B = -d_i^C \quad \forall i \quad (A16) \]
\[ d_i^D = -d_i^A \quad \forall i. \quad (A17) \]

The displacement of protons from the bond midpoint on the 8 sublattices of bonds are given by \( \pm a_i \), where

\[
\begin{align*}
    a_0 &= \phi d_0^A \\
    a_1 &= \phi d_1^A \\
    a_2 &= \phi d_2^A \\
    a_3 &= \phi d_3^A \\
    a_4 &= \phi d_0^C \\
    a_5 &= \phi d_1^C \\
    a_6 &= \phi d_2^C \\
    a_7 &= \phi d_3^C.
\end{align*}
\]

(A18)

For the purpose of our scattering calculations we take the size of the proton displacement from the bond midpoint relative to the bond length to be

\[ \phi = 0.15 \quad (A19) \]

assuming an O-H covalent bond length [60]

\[ a_{OH} = 0.95 \ \text{Å}. \quad (A20) \]

For the calculation of the dispersion of the lattice gauge theory, presented in Section [IV] and Appendix [E] it is necessary to define a labelling convention for the eight sets of oxygen–oxygen bonds not related by translational symmetries and for the eight sets six-link plaquettes. Our convention is defined in Fig. [I0]

Of particular are importance are the set of vectors which link the bond midpoints around the edge of a plaquette to the center of the plaquette. We denote these vectors \( c_{nm} \) where two bonds of sublattice \( m \) belong to a plaquette of sublattice \( n \) and are located at \( p_n \pm c_{nm} \) with the plaquette center being at \( p_n \). Where only one bond of sublattice \( m \) belongs to a plaquette of sublattice \( n \) we denote it’s position relative to the center of the plaquette by \( C_{nm} \). These vectors are

\[
\begin{align*}
    c_{01} &= -c_{10} = c_{45} = -c_{54} = a_0 \left( -\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{2}}, 0 \right) \\
    c_{02} &= -c_{20} = c_{46} = -c_{64} = a_0 \left( -\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{2}}, 0 \right) \\
    c_{03} &= -c_{30} = c_{47} = -c_{74} = a_0 \left( \frac{\sqrt{2}}{3}, 0, 0 \right) \\
    C_{12} &= C_{21} = a_0 \left( 0, \frac{\sqrt{2}}{3}, \frac{2}{3} \right) \\
    C_{13} &= C_{31} = a_0 \left( \frac{1}{\sqrt{6}}, -\frac{1}{3\sqrt{2}}, \frac{2}{3} \right) \\
    C_{23} &= C_{32} = a_0 \left( -\frac{1}{\sqrt{6}}, -\frac{1}{3\sqrt{2}}, \frac{2}{3} \right) \\
    C_{56} &= C_{65} = a_0 \left( 0, -\frac{\sqrt{2}}{3}, \frac{2}{3} \right) \\
    C_{57} &= C_{75} = a_0 \left( -\frac{1}{\sqrt{6}}, \frac{1}{3\sqrt{2}}, \frac{2}{3} \right) \\
    C_{67} &= C_{76} = a_0 \left( \frac{1}{\sqrt{6}}, \frac{1}{3\sqrt{2}}, \frac{2}{3} \right) \\
    C_{16} &= C_{25} = a_0 \left( 0, \frac{\sqrt{2}}{3}, -\frac{2}{3} \right) \\
    C_{17} &= C_{35} = a_0 \left( \frac{1}{\sqrt{6}}, -\frac{1}{3\sqrt{2}}, -\frac{2}{3} \right) \\
    C_{27} &= C_{36} = a_0 \left( -\frac{1}{\sqrt{6}}, -\frac{1}{3\sqrt{2}}, -\frac{2}{3} \right) \\
    C_{53} &= C_{71} = a_0 \left( -\frac{1}{\sqrt{6}}, \frac{1}{3\sqrt{2}}, -\frac{2}{3} \right) \\
    C_{63} &= C_{72} = a_0 \left( \frac{1}{\sqrt{6}}, \frac{1}{3\sqrt{2}}, -\frac{2}{3} \right) \\
    C_{61} &= C_{52} = a_0 \left( 0, -\frac{\sqrt{2}}{3}, -\frac{2}{3} \right)
\end{align*}
\]

Appendix B: Derivation of constraints within in continuum field–theory

In this Appendix we describe in detail the coarse–graining procedure used in Section [III] to obtain the constraint Eqs. (A16)–(A17).

The argument begins by setting \( m_r = 0 \) for all \( A \) and \( C \) vertices [cf. Fig. 2(b)]. If we then set the value of the total flux \( P_r \) around every \( A \) and \( C \) vertex, we have specified the H-bond configuration of the entire lattice. The necessity that this configuration must also obey \( m_r = 0 \) at the \( B \) and \( D \) vertices induces constraints on how \( P_r \) varies in space.

To derive those constraints in the long wavelength limit we introduce two coarse–grained fields \( P^A(r), P^C(r) \) defined at every point in space (not just on the lattice). We define \( P^A(r) \) in such way that when it is evaluated at the position of an
oxygen vertex of the $A$ sublattice, it returns the precise value of the total flux around that vertex

$$\mathbf{P}^A(r = \mathbf{r}_A) = \mathbf{P}_{\mathbf{r}_A}. \quad (B1)$$

Similarly

$$\mathbf{P}^C(r = \mathbf{r}_C) = \mathbf{P}_{\mathbf{r}_C}. \quad (B2)$$

To obtain our constraints on $\mathbf{P}^A(\mathbf{r})$, $\mathbf{P}^C(\mathbf{r})$ we write the scalar field $m_r$ at the $B$ and $D$ vertices in terms of the degrees of freedom at the four surrounding vertices.

A vertex of the $B$ sublattice [cf. Fig. 3], located at $\mathbf{r}_B$, neighbours one $A$ vertex located at

$$\mathbf{r}_A^{(0)} = \mathbf{r}_B - \mathbf{d}_0^A \quad (B3)$$

and three $C$ vertices located at

$$\mathbf{r}_C^{(i)} = \mathbf{r}_B - \mathbf{d}_i^C \quad i = 1, 2, 3 \quad (B5)$$

[cf. Eqs. (A9)-(A11)].

Using the vanishing of $m_r$ at the $A$ and $C$ vertices

$$m_{RB} = \frac{3}{4} \left\{ \sum_{i=1}^{3} \frac{1}{a^C_i} \mathbf{P}_{\mathbf{r}_B - \mathbf{d}_i^C} \mathbf{P}_{\mathbf{r}_B - \mathbf{d}_i^C} + P_{\mathbf{r}_B - \mathbf{d}_0^C} \right\} \quad (B6)$$

and similarly

$$m_{RD} = \frac{3}{4} \left\{ \sum_{i=1}^{3} \frac{1}{a^i_D} \mathbf{P}_{\mathbf{r}_D - \mathbf{d}_i^A} \mathbf{P}_{\mathbf{r}_D - \mathbf{d}_i^A} + P_{\mathbf{r}_D - \mathbf{d}_0^A} \right\} \quad (B7)$$

Assuming smooth variation of $\mathbf{P}^A(\mathbf{r})$, $\mathbf{P}^C(\mathbf{r})$ we can use a Taylor expansion to write

$$P_{r_{A,C}\delta r}^\alpha = P_{A,C}^\alpha(\mathbf{r}) + \delta \mathbf{r} \cdot \nabla P_{A,C}^\alpha(\mathbf{r}). \quad (B8)$$

Enforcing $m_{RB} = m_{RD} = 0$ throughout the lattice, we obtain the constraints on our continuum field–theory, Eq. (12)–(13).

**Appendix C: Projection operator calculation of structure factor for classical water ice**

Here we show how to calculate the structure factor for the Ising bond variables $\sigma_{\mathbf{r}\mathbf{r}'}$ [Eq. (31)] via a generalisation of the lattice calculation in Ref. 49. In this approximation the Ising nature of the variables $\sigma_{\mathbf{r}\mathbf{r}'}$ is relaxed, such that we can take on any real value and their normalisation is enforced on average

$$\langle \sigma_{\mathbf{r}\mathbf{r}'}^2 \rangle = 1. \quad (C1)$$

The calculation proceeds by constructing a projection operator which acts on the Fourier transform of an arbitrary proton configuration, to remove all states which do not satisfy the ice rules.

We begin by defining the Fourier transform over the bond variables as in Section III B [Eq. (30)], i.e.

$$\sigma_{\mathbf{r}\mathbf{r}'}(q) = \sqrt{\frac{1}{N}} \sum_{\mathbf{r}r'\in\nu} \exp(-i\mathbf{q} \cdot \mathbf{R}_{\mathbf{r}\mathbf{r}'}^\nu) \sigma_{\mathbf{r}\mathbf{r}'}^\nu, \quad (C2)$$

where $\nu$ indexes one of the eight sublattices of bonds which are not related by a translational symmetry of the lattice, and $\mathcal{N}$ counts the number of oxygen atoms. The sign of $\sigma_{\mathbf{r}\mathbf{r}'}^\nu$ is fixed by the convention [Eq. (30)]

$$\mathbf{r} \in \{A, C\}, \ r' \in \{B, D\}. \quad (C3)$$

We also introduce a net Ising polarisation for each oxygen sublattice $\alpha = A, B, C, D$,

$$m_\alpha(\mathbf{q}) = \sqrt{\frac{1}{N}} \sum_{\mathbf{r}\in\alpha} \exp(-i\mathbf{q} \cdot \mathbf{r}) m(\mathbf{r}). \quad (C4)$$

It follows from Eq. (8) that

$$m_\alpha(\mathbf{q}) = 0 \quad \forall \alpha, \mathbf{q} \quad (C4)$$

in any state obeying the ice rules.

The constraint Eq. (C4) can be written as a set of orthogonality conditions on $\tilde{\sigma}(\mathbf{q})$

$$\langle \tau_\alpha(\mathbf{q}), \tilde{\sigma}(\mathbf{q}) \rangle = 0, \ \alpha = A, B, C, D \quad (C5)$$

where the inner product

$$\langle A, B \rangle = \sum_i A_i B_i \quad (C6)$$

and the 8-component vectors $\tau_\alpha(\mathbf{q})$ are defined by

$$\tau_A = (e^{i\mathbf{q} \cdot \mathbf{d}_0^A/2}, e^{i\mathbf{q} \cdot \mathbf{d}_1^A/2}, e^{i\mathbf{q} \cdot \mathbf{d}_2^A/2}, e^{i\mathbf{q} \cdot \mathbf{d}_3^A/2}, 0, 0, 0, 0) \quad (C7)$$

$$\tau_B = (e^{i\mathbf{q} \cdot \mathbf{d}_0^B/2}, 0, 0, 0, 0, e^{i\mathbf{q} \cdot \mathbf{d}_1^B/2}, e^{i\mathbf{q} \cdot \mathbf{d}_2^B/2}, e^{i\mathbf{q} \cdot \mathbf{d}_3^B/2}) \quad (C8)$$

$$\tau_C = (0, 0, 0, 0, e^{i\mathbf{q} \cdot \mathbf{d}_0^C/2}, e^{i\mathbf{q} \cdot \mathbf{d}_1^C/2}, e^{i\mathbf{q} \cdot \mathbf{d}_2^C/2}, e^{i\mathbf{q} \cdot \mathbf{d}_3^C/2}) \quad (C9)$$

$$\tau_D = (0, e^{i\mathbf{q} \cdot \mathbf{d}_0^D/2}, e^{i\mathbf{q} \cdot \mathbf{d}_1^D/2}, e^{i\mathbf{q} \cdot \mathbf{d}_2^D/2}, e^{i\mathbf{q} \cdot \mathbf{d}_3^D/2}, 0, 0, 0) \quad (C10)$$
with the vector \( \mathbf{d}_\alpha \) defined in Eqs. (A9)–(A17).

At long wavelength (i.e. in the vicinity of a Brillouin zone center), the orthogonality conditions Eqs. (C7)–(C10) must reduce to the constraints on the classical fields \( P_+ \) and \( P_- \), discussed Section III A and Appendix B. The connection between the two approaches can be made explicit by rewriting the constraints on bond variables, Eqs. (C7)–(C10), in terms of the lattice variable \( m_\alpha \) and \( P_\tau \). To this end we introduce the Fourier transform of the polarization \( P_\tau \) on sublattice \( \alpha \)

\[
P_\alpha(q) = \sqrt{4/N} \sum_{\mathbf{r} \in \alpha} \exp(-i\mathbf{q} \cdot \mathbf{r}) P_\tau , \quad (C11)
\]

For the moment, we restrict our discussion to wavevectors \( q \) which are close to a reciprocal lattice vector \( Q \) and write

\[
q = Q + \tilde{q} \quad (C12)
\]

By analogy with Eqs. (14)–(15) of the main text, we write

\[
m_\pm(\tilde{q}) = \frac{1}{\sqrt{2}} \left[ \exp(iQ \cdot r_A) m_A(q) \pm \exp(iQ \cdot r_C) m_C(Q + \tilde{q}) \right] \quad (C13)
\]

\[
P_\pm(\tilde{q}) = \frac{1}{\sqrt{2}} \left[ \exp(iQ \cdot r_A) P_A(Q + \tilde{q}) \pm \exp(iQ \cdot r_C) P_C(Q + \tilde{q}) \right] . \quad (C14)
\]

The vectors \( r_A \) and \( r_C \) are the positions of the oxygen sites labelled \( A \) and \( C \) within a primitive unit cell. Note that we have defined the fields in Eqs. (C13) and (C14) in such a way that they are independent of the reciprocal lattice vector \( Q \) and depend only on the distance to the zone center \( \tilde{q} \). We may therefore use Eqs. (20)–(22), with the replacement

\[
q \to \tilde{q} \quad (C15)
\]

to describe the correlations at small \( \tilde{q} \) in the vicinity of all reciprocal lattice vectors \( Q \), i.e. near all Brillouin zone centers.

To demonstrate that the constraints derived in the continuum theory [Eqs. (16)–(17)] are equivalent to the constraints in the lattice theory [Eq. (C5)] in the limit \( \tilde{q} \to 0 \) we consider the following linear combinations of the vectors

\[
\tau(q) = \tau(Q + \tilde{q})
\]

\[
\tau_{AC+}(Q, \tilde{q}) = \frac{1}{\sqrt{2}} \left[ \exp(iQ \cdot r_A) \tau_A(Q + \tilde{q}) + \exp(iQ \cdot r_C) \tau_C(Q + \tilde{q}) \right] \quad (C16)
\]

\[
\tau_{AC-}(Q, \tilde{q}) = \frac{1}{\sqrt{2}} \left[ \exp(iQ \cdot r_A) \tau_A(Q + \tilde{q}) - \exp(iQ \cdot r_C) \tau_C(Q + \tilde{q}) \right]
\]

\[
\tau_{BD+}(Q, \tilde{q}) = \frac{1}{\sqrt{2}} \left[ \exp(iQ \cdot r_B) \tau_B(Q + \tilde{q}) + \exp(iQ \cdot r_D) \tau_D(Q + \tilde{q}) \right] \quad (C17)
\]

\[
\tau_{BD-}(Q, \tilde{q}) = \frac{1}{\sqrt{2}} \left[ \exp(iQ \cdot r_B) \tau_B(Q + \tilde{q}) - \exp(iQ \cdot r_D) \tau_D(Q + \tilde{q}) \right] \quad (C18)
\]

where \( r_A, r_B, r_C \) and \( r_D \) are the positions of each oxygen vertex in the unit cell.

We can then express the constraints on \( \hat{\sigma}(q) \) [Eq. (C5)] as

\[
(\tau_{AC+}(Q, \tilde{q}), \hat{\sigma}(Q + \tilde{q})) = 0 \quad (C20)
\]

\[
(\tau_{AC-}(Q, \tilde{q}), \hat{\sigma}(Q + \tilde{q})) = 0 \quad (C21)
\]

\[
(\tau_{BD+}(Q, \tilde{q}), \hat{\sigma}(Q + \tilde{q})) = 0 \quad (C22)
\]

\[
(\tau_{BD-}(Q, \tilde{q}), \hat{\sigma}(Q + \tilde{q})) = 0 \quad (C23)
\]

Since

\[
(\tau_{AC+}(Q, \tilde{q}), \hat{\sigma}(Q + \tilde{q})) = m_+(\tilde{q}) \quad (C24)
\]

\[
(\tau_{AC-}(Q, \tilde{q}), \hat{\sigma}(Q + \tilde{q})) = m_-(\tilde{q}) \quad (C25)
\]

the constraints Eq. (C20) and Eq. (C21) are satisfied if

\[
m_+(\tilde{q}) = m_-(\tilde{q}) = 0 \quad (C26)
\]

The constraints on \( \tau(Q, \tilde{q}) \), Eq. (C22) and Eq. (C23), give rise to constraints on the \( q \) dependence of \( P_+ (\tilde{q}) \) and \( P_- (\tilde{q}) \). Reexpressing Eq. (C22) in terms of \( P_+ (\tilde{q}) \) [Eq. (14)] and \( P_- (\tilde{q}) \) [Eq. (15)], and expanding to linear order in \( \tilde{q} \) we find

\[
\tilde{q} \cdot P_+(\tilde{q}) + O(q^2) = 0 \quad (C27)
\]

This precisely the Fourier transform of Eq. (16), i.e. the required condition on \( P_+ \). Similarly, Eq. (C23) becomes

\[
P_-^z(\tilde{q}) + \alpha_0 \left( P^-_z(\tilde{q}) + q_z P^-_z(\tilde{q}) \right) + O(q^2) = 0 \quad (C28)
\]

which is the Fourier transform of Eq. (17).

Having established that the lattice–based theory is equivalent to the continuum field theory at long wavelength, we now turn to the problem of calculating the structure factors which describe proton–proton correlations for arbitrary \( q \). Within the lattice–based theory, this reduces to constructing a matrix \( P \) which projects states into the subspace of proton configurations orthogonal to the set of vectors \( \tau_\alpha(q) \). Explicit construction of \( P \) is messy, and the final expression for the structure factor must be evaluated numerically.
We proceed by using Gram-Schmidt orthogonalisation to construct from \( \{ \tau_\alpha(q) \} \) an orthogonal basis \( \{ \tau_\alpha(q) \}' \):

\[
\tau'_A = \tau_A \\
\tau'_B = \tau_B - \frac{(\tau_B, \tau'_A)}{(\tau'_A, \tau'_A)} \tau'_A \\
\tau'_C = \tau_C - \frac{(\tau_C, \tau'_A)}{(\tau'_A, \tau'_A)} \tau'_A - \frac{(\tau_C, \tau'_B)}{(\tau'_B, \tau'_B)} \tau'_B \\
\tau'_D = \tau_D - \frac{(\tau_D, \tau'_A)}{(\tau'_A, \tau'_A)} \tau'_A - \frac{(\tau_D, \tau'_B)}{(\tau'_B, \tau'_B)} \tau'_B - \frac{(\tau_D, \tau'_C)}{(\tau'_C, \tau'_C)} \tau'_C
\]

(C29) (C30) (C31) (C32)

The projection matrix \( P(q) \) is then given by

\[
P_{ij}(q) = \delta_{ij} - \sum_{\alpha} \frac{\tau_{\alpha i}' \tau_{\alpha j}'}{(\tau_{\alpha i}', \tau_{\alpha j}')} \tag{C33}
\]

The structure factor is obtained by acting on the Fourier transform of some general (non-ice rule obeying) state \( \hat{\sigma}'(q) \)

\[
\langle \sigma_i(-q) \sigma_j(q) \rangle = \\
= \sum_{mn} P_{in}(-q) P_{jm}(q) \langle \sigma_i'(-q) \sigma_j'(q) \rangle \\
= \sum_{mn} N_0 \delta_{mn} P_{in}(-q) P_{jm}(q) \\
= N_0 P_{ij}(q)
\]

where \( N_0 \) is a normalisation constant and in the last step we have used the identities

\[
P(-q) = P(q)^* \\
P(q)^* = P(q)^T \\
P(q)^2 = P(q)
\]

(C35) (C36) (C37)

The constant \( N_0 \) is fixed by Eq. (C1). This method was used to calculate the scattering patterns in Figs. 5 and 6.

Appendix D: Relating structure factors to correlations of \( P_+(q) \) and \( P_-(q) \)

In this Appendix we derive the relationship between the structure factors \( S_{\text{Ising}}(q) \) and \( S_{\text{diffuse}}(q) \), discussed in Section III and Section III C of the main text, and the correlation functions of the fields \( P_\pm(q) \), introduced in Section III A. In so doing we establish the necessary conditions for a zone centre to exhibit singular, pinch–point scattering.

The structure factors \( S_{\text{Ising}}(q) \) [Eq. (28)] and \( S_{\text{diffuse}}(q) \) [Eq. (44)] can both be expressed in terms of the correlations of the Ising variable \( \sigma(q) \) [Eq. (29)], as

\[
S_\chi(q) = \sum_{\nu, \nu'} \langle \sigma_\nu(q) \sigma_{\nu'}(-q) \rangle \eta_\nu'^{(\chi)}(q) \eta_\nu(q)(-q) \tag{D1}
\]

where

\[
\chi = \text{Ising} \quad \text{proton} \quad \text{D2}
\]

the sum on \( \nu \) runs over all bonds within the unit cell, and the coefficients \( \eta_\nu^{(\chi)}(q) \) depend on which structure factor is being calculated. In the case of \( S_{\text{Ising}}(q) \)

\[
\eta_\nu^{(\text{Ising})}(q) = 1 \quad \forall \nu, q \tag{D3}
\]

while for \( S_{\text{diffuse}}(q) \)

\[
\eta_\nu^{(\text{proton})}(q) = i \sin(q \cdot a_\nu) \tag{D4}
\]

The expression for \( S_\chi(q) \) [Eq. (D1)] can be factorised to give

\[
S_\chi(q) = \langle \sum_{\nu} \eta_\nu^{(\chi)}(q) \sigma_\nu(q) \rangle^2 \tag{D5}
\]

We are interested in understanding the behaviour of this structure factor near to a given reciprocal lattice vector \( Q \), in terms of the continuum field theory developed in Section III A. To this end, we write

\[
q = Q + \tilde{q} \tag{D6}
\]

and express \( S_\chi(q) \) in terms of the fields \( m_\pm(\tilde{q}) \) [Eq. (C13)] and \( P_{\pm}(\tilde{q}) \) [Eq. (C14)], to obtain

\[
\sum_{\nu} \eta_\nu^{(\chi)}(Q + \tilde{q}) \sigma_\nu(Q + \tilde{q}) = m_+^{(\chi)}(Q, \tilde{q}) m_-^{(\chi)}(Q, \tilde{q}) + \lambda_+^{(\chi)}(Q, \tilde{q}) \cdot P_+(\tilde{q}) + \lambda_-^{(\chi)}(Q, \tilde{q}) \cdot P_-(\tilde{q}) \tag{D7}
\]

where the vectors \( \lambda_{\pm}^{(\chi)}(Q, \tilde{q}) \) are defined in Eq. (D13) and Eq. (D14), below, and the scalar functions \( \mu_{\pm}^{(\chi)}(Q, \tilde{q}) \) play no part in our subsequent discussion.

In any state obeying the ice rules

\[
m_+(\tilde{q}) = m_-(-\tilde{q}) = 0 \tag{D8}
\]

so terms in these fields can safely be dropped

\[
\sum_{\nu} \eta_\nu^{(\chi)}(Q + \tilde{q}) \sigma_\nu(Q + \tilde{q}) = \lambda_+^{(\chi)}(Q, \tilde{q}) \cdot P_+(\tilde{q}) + \lambda_-^{(\chi)}(Q, \tilde{q}) \cdot P_-(\tilde{q}) \tag{D9}
\]

It follows that, for \(|\tilde{q}| \ll 1 \), the structure factor \( S_\chi(q) \) [Eq. D5] can be written as

\[
S_\chi(Q + \tilde{q}) \approx \sum_{\nu, \pm} F_\nu^{(\chi)}(Q) \langle |\hat{\lambda}_{Q, \nu}^{(\chi)} \cdot P_\nu(\tilde{q})| |^2 \rangle \tag{D10}
\]

where \( \hat{\lambda}_{Q, \nu}^{(\chi)} \) is a unit vector in the direction of

\[
\lambda_{Q, \nu}^{(\chi)} = \lambda_{\nu}^{(\chi)}(Q, \tilde{q} = 0) \tag{D11}
\]

[cf. Eq. (D13) and Eq. (D14)], and the form factor

\[
F_\nu^{(\chi)}(Q) = |\hat{\lambda}_{Q, \nu}^{(\chi)}|^2 \tag{D12}
\]

The final result for the structure factor, Eq. (D10), is strikingly simple. We learn that, evaluated near to a reciprocal
lattice vector $\mathbf{Q}$, the structure factor $S_\chi(q)$ measures correlations of both $\mathbf{P}_+(q)$ and $\mathbf{P}_-(q)$, where each is projected onto the vector $\hat{\lambda}^\chi_{Q,+}$ and $\hat{\lambda}^\chi_{Q,-}$, respectively. These correlations are mixed with a weight controlled by the form factors $F_\chi^+(Q)$ and $F_\chi^-(Q)$. The form factors are, in turn, fully determined by the vectors $\hat{\lambda}^\chi_{Q,+}$ and $\hat{\lambda}^\chi_{Q,-}$. These vectors therefore control both the “selection rules” which determine which of the fields $\mathbf{P}_+$ and $\mathbf{P}_-$ is manifest in the scattering around a given reciprocal lattice vector, and the way in which these fields couple to a given experimental probe.

All that remains is to substitute the appropriate $\lambda^\chi_{Q,+}$ in the expression for $S_\chi(q)$ [Eq. (D10)], using Eq. (D11). In the specific case of the Ising structure factor $S_{\text{Ising}}(q)$ [Eq. (28)], we have

$$\lambda^\text{Ising}_\chi(Q, q) = \exp(-iQ \cdot r_A) \sum_{i=0}^{3} \frac{3}{4a_0} d^A_i \exp[-i(Q + \tilde{q}) \cdot d^C_i/2]$$
$$\pm \exp(-iQ \cdot r_C) \sum_{i=0}^{3} \frac{3}{4a_0} d^C_i \exp[-i(Q + \tilde{q}) \cdot d^C_i/2],$$

(D13)

where the vectors $d^A_i$, $d^C_i$ are given in Eqs. (A9)–(A15).

Meanwhile, for the proton structure factor $S^\text{diffuse}_{\text{proton}}(q)$ [Eq. (44)], we have

$$\lambda^\text{proton}_\chi(Q, q) = \exp(-iQ \cdot r_A) \sum_{i=0}^{3} \frac{3}{4a_0} d^A_i \exp[-i(Q + \tilde{q}) \cdot d^C_i/2]$$
$$\times i \sin[\phi(Q + \tilde{q} \cdot d^4_i)]$$
$$\pm \exp(-iQ \cdot r_C) \sum_{i=0}^{3} \frac{3}{4a_0} d^C_i \exp[-i(Q + \tilde{q}) \cdot d^C_i/2]$$
$$\times i \sin[\phi(Q + \tilde{q} \cdot d^C_i)],$$

(D14)

where the parameter

$$\phi = 0.15$$

(D15)

expresses the relative displacement of the protons from the midpoint of the bond, as defined in Eq. (A19).

Appendix E: Calculation of the dispersion of emergent photons on the $Ih$ water ice lattice

The Hamiltonian of the $U(1)$ gauge theory on the pyroclore lattice is

$$\mathcal{H}_{U(1)} = \frac{U}{2} \sum_{(rr') \in CS} E_{rr'}^2 + \frac{U'}{2} \sum_{(rr') \in MS} E_{rr'}^2$$
$$\frac{K}{2} \sum_{(rr') \in CS} |\nabla_Q \times A|^2 + \frac{K'}{2} \sum_{(rr') \in MS} |\nabla_Q \times A|^2$$

(E1)

where the sum $\sum_{(rr') \in CS}$ runs over centre symmetric oxygen–oxygen bonds, $\sum_{(rr') \in MS}$ runs over mirror symmetric oxygen–oxygen bonds [cf. Fig. 3], $\sum_{r \in I}$ runs over plaquettes normal to the optical axis and $\sum_{r \in I}$ runs over plaquettes parallel to the optical axis [cf. Eq. (4)]. We may condense this as

$$\mathcal{H}_h = \frac{U}{2} \sum_{r} \sum_{m} \alpha_m E_{r_m}^2$$
$$+ \frac{K}{2} \sum_{r} \sum_{p} \beta_p [\nabla_Q \times A]_{r,p}^2$$

where $\sum_r$ is a sum over primitive unit cells and the sums over $m$ and $p$ are over bond and plaquette midpoints in a single unit cell respectively. For the eight component objects $\alpha$ and $\beta$ we have

$$\alpha = \left(1, 1, 1, \frac{U}{U'}, 1, 1, 1, \frac{U'}{U'} \right)$$
$$\beta = \left(\frac{K}{K'}, \frac{K'}{K}, \frac{K'}{K}, \frac{K'}{K}, \frac{K'}{K}, \frac{K'}{K}, \frac{K'}{K}, \frac{K'}{K} \right).$$

(E4)

We will use the notation

$$E_{(r,m)} = E_{r,r+d_m}$$
$$A_{(r,m)} = A_{r,r+d_m}$$

(E5)

(E6)

where $d_m$ is a bond vector in the direction of one of the eight inequivalent bonds in the unit cell.

We need now to write down an decomposition of these fields in terms of photon operators. This is

$$A_{(r,m)} = \sqrt{\frac{4}{N}} \sum_{k} \sum_{\lambda=1}^{8} \sqrt{\frac{\omega_{\lambda}(k)}{\omega_{\lambda}(k)}} \times$$
$$\left( \exp[-i \mathbf{k} \cdot (\mathbf{r} + d_m/2)] \eta_{\alpha}(k) \lambda(k) \right)$$
$$+ \exp[i \mathbf{k} \cdot (\mathbf{r} + d_m/2)] \eta_{\alpha}^*(k) \lambda(k)$$

(E7)

$$E_{(r,m)} = i \sqrt{\frac{4}{N}} \sum_{k} \sum_{\lambda=1}^{8} \sqrt{\frac{\omega_{\lambda}(k)}{\omega_{\lambda}(k)}} \times$$
$$\left( \exp[-i \mathbf{k} \cdot (\mathbf{r} + d_m/2)] \eta_{\alpha}(k) \lambda(k) \right)$$
$$- \exp[i \mathbf{k} \cdot (\mathbf{r} + d_m/2)] \eta_{\alpha}^*(k) \lambda(k)$$

(E8)

It is easy to check that that Eqs. (E7)–(E8) fulfill the commutation relationship

$$[E_{(r,m)}, A_{(r,m)}] = i.$$

(E9)

As in Ref. [33], we may write $\nabla_Q A_{(r,m)}$ in terms of our Fourier decomposition as a matrix $\mathbb{A}(k)$ acting on the vectors $\eta_{\lambda}(k)$. 

We have

\[
\sqrt{\beta_p} (\nabla \times A)_{(r,p)} = \sqrt{\frac{4}{N}} \sum_k \sum_{\lambda=1}^4 \frac{\beta_p}{\omega_\lambda(k)} \left\{ \exp[-i k \cdot (r_p)]a_\lambda(k) \sum_m \sqrt{\beta_p Z_{pm}(k)} \sqrt{\alpha_m} \eta_{\lambda m}(k) \right. \\
+ \left. \exp [i k \cdot (r_p)] a_\lambda(k) \sum_m \eta_{\lambda m} \sqrt{\beta_p Z_{pm}(k)^*} \sqrt{\alpha_m} \right\},
\]

(E10)

The matrix \(Z(k)\) is

\[
Z(k) =
\begin{pmatrix}
0 & 2i \sin(k \cdot c_{01}) & 2i \sin(k \cdot c_{02}) & 2i \sin(k \cdot c_{03}) & 0 & 0 & 0 & 0 \\
2i \sin(k \cdot c_{10}) & 0 & e^{-ik C_{12}} & e^{-ik C_{13}} & 0 & 0 & e^{-ik C_{16}} & e^{-ik C_{17}} \\
2i \sin(k \cdot c_{20}) & e^{-ik C_{21}} & 0 & e^{-ik C_{23}} & 0 & 0 & -e^{-ik C_{25}} & 0 \\
2i \sin(k \cdot c_{30}) & e^{-ik C_{31}} & e^{-ik C_{32}} & 0 & 0 & e^{-ik C_{35}} & 0 & -e^{-ik C_{27}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & e^{-ik C_{61}} & 0 & e^{-ik C_{63}} & 0 & 0 & 2i \sin(k \cdot c_{54}) & 2i \sin(k \cdot c_{56}) \\
0 & e^{-ik C_{62}} & 0 & e^{-ik C_{63}} & 0 & 0 & 2i \sin(k \cdot c_{54}) & 2i \sin(k \cdot c_{56}) \\
0 & e^{-ik C_{71}} & e^{-ik C_{72}} & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

Where the vectors \(c_m, C_{nm}\) are vectors joining the central points of plaquettes to the bond midpoints around the outside. These vectors are defined in Appendix[A] along with the numbering convention for sites and plaquettes.

Defining

\[
Y_{mp}(k) = \sqrt{\alpha_m}Z_{mp}(k) \sqrt{\beta_p}
\]

(E11)
we may write
\[ \sqrt{\beta_p} (\nabla \times A)_{\mathbf{r},p} = \sqrt{\frac{4}{N}} \sum_{\mathbf{k}} \sum_{\lambda=1}^4 \sqrt{\frac{U}{\omega_\lambda(\mathbf{k})}} \]
\[ \times \left\{ \exp[-i\mathbf{k} \cdot \mathbf{r}_p]a_\lambda(\mathbf{k}) \right. \times \sum_m Y_{pm}(\mathbf{k})\eta_{m\lambda}(\mathbf{k}) \]
\[ + \exp[i\mathbf{k} \cdot \mathbf{r}_p]a_\lambda^\dagger(\mathbf{k}) \times \sum_m \eta_{m\lambda}^* Y_{m\lambda}^*(\mathbf{k}) \right\}. \quad \text{(E12)} \]

The matrix \( Y(k) \) is not guaranteed to be Hermitian, so we cannot necessarily form an orthonormal set of vectors \( \eta_\lambda(k) \) from its eigenvectors. However, the matrix \( Y^\dagger(k) \cdot Y(k) \) is Hermitian and has positive semi-definite eigenvalues, so we may write
\[ Y^\dagger(k) \cdot Y(k) \eta_\lambda(k) = \zeta_\lambda(k)^2 \eta_\lambda(k). \quad \text{(E13)} \]

Squaring and summing over \( r \) and \( p \) we have
\[ \frac{K}{2} \sum_r \sum_p \beta_p \left[ (\nabla \times A)_{\mathbf{r},p} \right]^2 = \frac{UK}{4} \sum_{\mathbf{k}} \sum_{\lambda} \frac{\zeta_\lambda(k)^2}{\omega_\lambda(k)} \left\{ a_\lambda(\mathbf{k})a_\lambda(-\mathbf{k}) + a_\lambda^\dagger(\mathbf{k})a_\lambda^\dagger(-\mathbf{k}) \right. \]
\[ + a_\lambda^\dagger(\mathbf{k})a_\lambda(\mathbf{k}) + a_\lambda(\mathbf{k})a_\lambda^\dagger(\mathbf{k}) \right\}. \quad \text{(E14)} \]

Similarly
\[ \frac{U}{2} \sum_{(e,m)} a_m(E_{em})^2 = \frac{1}{4} \sum_{\mathbf{k}} \sum_{\lambda=1}^4 \omega_\lambda(k) \left\{ - a_\lambda(\mathbf{k})a_\lambda(-\mathbf{k}) - a_\lambda^\dagger(\mathbf{k})a_\lambda^\dagger(-\mathbf{k}) \right. \]
\[ + a_\lambda^\dagger(\mathbf{k})a_\lambda(\mathbf{k}) + a_\lambda(\mathbf{k})a_\lambda^\dagger(\mathbf{k}) \right\}. \quad \text{(E15)} \]

Inserting this into the Hamiltonian [Eq. (E11)] results in
\[ \mathcal{H}_{\text{inh}} = \sum_{\mathbf{k}} \sum_{\lambda=1}^8 \omega_\lambda(\mathbf{k}) \left( a_\lambda^\dagger(\mathbf{k})a_\lambda(\mathbf{k}) + \frac{1}{2} \right) \quad \text{(E16)} \]

where the dispersion \( \omega_\lambda(k) \) is fixed by requiring the off-diagonal terms to vanish
\[ \omega_\lambda(k) = \sqrt{UK} |\zeta_\lambda(k)|. \quad \text{(E17)} \]

The functions \( \zeta_\lambda(k) \) are found by numerical diagonalization of \( Y^\dagger(k) \cdot Y(k) \). Four of the modes \( \lambda \) are unphysical, zero-energy modes (cf. the two unphysical zero energy modes which occur in the pyrochlore case [33]). The remaining four modes are now non-degenerate, which is again in contrast to the cubic symmetry case. Two of these modes are gapless and linearly dispersing and therefore recognisable as photons, while the other two modes are gapped and are associated with quantised fluctuations of the classical field \( P_- \) (see Section III). The identification of the gapless modes with fluctuations of \( P_+ \) and the gapped modes with fluctuations of \( P_- \) is illustrated in Fig. [11].

The time evolution of the electromagnetic fields is given by the time evolution of the photon operators \( a_\lambda(q), a_\lambda^\dagger(q) \), which, since the photons are eigenstates of \( \mathcal{H}_{\text{inh}} \), is simply
\[ a_\lambda(q)(t) = e^{i\omega_\lambda(q)t}a_\lambda(q)(0) \quad a_\lambda^\dagger(q)(t) = e^{-i\omega_\lambda(q)t}a_\lambda^\dagger(q)(0). \quad \text{(E18)} \]

Therefore
\[ E_m(q,\omega) = \frac{i}{2} \sum_{\lambda} \sqrt{\omega_\lambda(q)} \left( \eta_{m\lambda}(q)a_\lambda(\omega)e^{-i\omega_\lambda(q)t} + \eta_{m\lambda}^*(q)e^{i\omega_\lambda(q)t}a_\lambda^\dagger(q) \right) \quad \text{(E19)} \]

and the dynamical structure factor for the electric fields is
\[ S_Q^{\pm m}(q,\omega) = \int dt e^{-i\omega t} \left\langle E_m(-q,0)E_{m,-q}(q,t) \right\rangle \]
\[ = \frac{1}{2} \sum_{\lambda} \left[ \delta(\omega - \omega_\lambda(q)) (1 + n_B(\omega)) + \delta(\omega + \omega_\lambda(q)) n_B(\omega) \right] \frac{\omega_\lambda(q)}{\alpha_m\omega_\lambda} \eta_{m\lambda}^* \eta_{m\lambda} \quad \text{(E20)} \]

The correlations functions of the electric field relate directly to the structure factor for coherent scattering of neutrons which is [81]
\[ S_{\text{coh}}(q,\omega) = \frac{1}{2\pi} \sum_j \sum_{j'} \int_{-\infty}^{\infty} dt e^{-i\omega t} \times \langle \exp(-iq \cdot R_j(0)) \exp(iq \cdot R_{j'}(t)) \rangle \quad \text{(E21)} \]

Within the treatment of the proton dynamics presented here, the diffuse contribution to this is given by
\[ S_{\text{diff}}(q,\omega) = \sum_{m,n} \sin(q \cdot a_m) \sin(q \cdot a_n) S_Q^{\pm m}(q,\omega) \quad \text{(E22)} \]

where \( m,n \) index the eight sublattices of bonds and the displacement of a proton from the bond midpoint of bond \( m \) is \( \pm a_m \).

We have also calculated the structure factor of the fields \( P_+(r) \) and \( P_-(r) \) [Fig. [11]]. To do this we define we write in analogy with Eq. [C14] for the fields \( P_\pm(q) \) for wavevector \( q = Q + \tilde{q} \) in a Brillouin zone centred on reciprocal lattice vector \( Q \)
\[ P_\pm(q,\omega) = \sqrt{\frac{4}{N}} \int_{-\infty}^{\infty} \exp(-i\omega t) \times \left[ \exp(iQ \cdot r_A) \sum_{r \in A} \exp(-iq \cdot r) P_\pm(r_A, t) + \exp(iQ \cdot r_C) \sum_{r \in C} \exp(-iq \cdot r) P_\pm(r_C, t) \right] \quad \text{(E23)} \]
FIG. 12. (Color online). Ising structure factor $S_{\text{Ising}}(\mathbf{q})$ [Eq. (28)] for a classical model of $Ih$ water ice, calculated from classical Monte Carlo simulation [(a)-(c)] and from lattice theory [(d)-(f)]. The theory calculation is performed using the method outlined in Appendix C which is based on the method described for spin ice in Ref. 49. This method consists in writing the ice rule constraints as orthogonality conditions in Fourier space. In the long wavelength limit these conditions reduce to those obtained from the continuum field–theory presented in Section III A [Eqs. (16)-(17)]. Near the zone centres the correlations are well described by a combination of pinch point singularities, reflecting the algebraic correlations of $P_+ (\mathbf{q})$ and smooth features reflecting the short ranged correlations of $P_- (\mathbf{q})$.

where we have chosen a definition such that $P_{\pm} (\mathbf{q}, \omega)$ is the same in all Brillouin zones. The vectors $\mathbf{r}_A, \mathbf{r}_C$ are the positions of the $A$ and $C$ oxygen vertices within a primitive unit cell.

Restricting the sum to the $A$ and $C$ sublattices of oxygen ions means that each bond only contributes to the sum once. In Fig. 11 we plot $\langle P_+ (-\mathbf{q}, -\omega) \cdot P_+ (\mathbf{q}, \omega) \rangle$ and $\langle P_- (-\mathbf{q}, -\omega) \cdot P_- (\mathbf{q}, \omega) \rangle$. At long wavelengths we can see directly from Fig. 11 that the correlations of $P_+$ are directly associated with the gapless photon modes and that fluctuations of $P_-$ are gapped.

Appendix F: Comparison with numerics

1. Classical Monte Carlo simulation

In this Appendix we compare our calculations of the correlation functions in the classical ice problem with the results of Monte Carlo simulations for a cluster of 1024 oxygen–oxygen bonds.

To obtain numerical results for the correlations in the absence of quantum tunnelling it is necessary to take an equally weighted average over ice rule configurations. This is accomplished numerically by starting from a configuration with zero total electric polarisation and then acting randomly with the hexagonal ring exchange operators [cf. Eq. (4)] to generate new configurations. Since these operations preserve total electric polarisation the average obtained in this way only includes states of vanishing total polarisation. However, this set of states is representative of the manifold as a whole, as in the case of spin ices.

In Fig. 12 we compare results for the Ising structure factor $S_{\text{Ising}}(\mathbf{q})$ [Eq. (28)] between these Monte Carlo calculations [(a)-(c)] and the projection method outlined in Appendix C [(d)-(f)]. Noticeable differences are visible for $\mathbf{q}$ located exactly at Brillouin zone centers. This is caused by the restriction to states of vanishing total polarisation in the simulations.
However, for any \( \mathbf{q} \) not exactly at a Brillouin zone center there is very good agreement between the theory calculation and Monte Carlo, strongly validating our understanding of the classical ice problem.

2. Quantum Monte Carlo simulation

In order to validate our description of quantum \( Ih \) water ice, we have compared the predictions of the lattice gauge theory \( \mathcal{H}_{U(1)} \) [Eq. (65)] for equal–time correlation functions, with the results of variational quantum Monte Carlo (VMC) simulations of the microscopic model \( \mathcal{H}^{\text{honeycomb}} \) [Eq. (4)].

VMC simulations were carried out for an orthorhombic cluster of 1024 oxygen–oxygen bondswith a one-parameter variational wavefunction of the form

\[
|\psi_{\alpha}^{\text{var}}\rangle = \exp(\alpha N_f) |\psi_0\rangle
\]

where the operator \( N_f \) measures the number “flippable” plaquettes (of both type I and II), \( \alpha \) is a variational parameters, and \( |\psi_0\rangle \) is an equal weight superposition of all ice configurations within a given flux–sector of the Hilbert space. This variational wave function correctly describes the liquid phase of the microscopic model [Eq. (4)], and variational Monte Carlo [33, 40]. A field-renormalization of \( S^z \), allowed in principle within the lattice gauge theory [32, 33], has also been set equal to one.

The agreement between the results of the two methods is excellent, confirming that the lattice gauge theory correctly describes the liquid phase of the microscopic model.

Appendix G: Calculation of the incoherent scattering cross section

The structure factor for inelastic, incoherent, neutron scattering from a set of nuclei at located at positions \( \mathbf{R}_j \) is

\[
S_{\text{inc}}(\mathbf{q}, \omega) = \frac{1}{2\pi} \sum_j \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \exp(-i\mathbf{q} \cdot \mathbf{R}_j(0)) \exp(i\mathbf{q} \cdot \mathbf{R}_j(t)) \rangle
\]

We approximate the position of the proton on bond \( j \) of the lattice, \( \mathbf{R}_j(t) \), to be given by

\[
\mathbf{R}_j(t) = \mathbf{r}_j^0 + \mathbf{a}_j \sigma_j(t)
\]

where \( \mathbf{r}_j^0 \) is the bond midpoint, \( \mathbf{a}_j \) describes the displacement of the two proton sites on the bond from the bond midpoint and \( \sigma_j(t) = \pm 1 \) is the Ising variable describing the bond polarisations.

Since \( \sigma_j(t) = \pm 1 \) and \( \mathbf{r}_j^0 \) and \( \mathbf{a}_j \) are constants we can write

\[
\exp(i\mathbf{q} \cdot \mathbf{R}_j(t)) = \exp(i\mathbf{q} \cdot \mathbf{r}_j^0) \left[ \cos(\mathbf{q} \cdot \mathbf{a}_j) + i\sigma_j(t) \sin(\mathbf{q} \cdot \mathbf{a}_j) \right]
\]
Since
\[ \langle \sigma_j(t) \rangle = 0 \quad (G4) \]
on inserting Eq. (G3) into Eq. (G1) we obtain two terms, corresponding to the elastic and inelastic contributions to the incoherent scattering
\[ S_{\text{inc}}(q, \omega) = S_{\text{inc,el}}(q, \omega) + S_{\text{inc,inel}}(q, \omega) \quad (G5) \]
The elastic contribution is simply
\[ S_{\text{inc,el}}(q, \omega) = \delta(\omega) \sum_j \cos^2(q \cdot a_j) \quad (G6) \]
while the inelastic contribution is
\[ S_{\text{inc,inel}}(q, \omega) = \sum_j \sin^2(q \cdot a_j) \langle \sigma_j(-\omega)\sigma_j(\omega) \rangle \quad (G7) \]
For the purposes of comparison with experiments we need to integrate the momentum transfer dependence over angle, which gives
\[ S_{\text{inc,el}}^\text{pow}(Q, \omega) = \delta(\omega) \sum_j \frac{1}{2} \left( 1 + \frac{\sin(2Q|a_j|)}{2Q|a_j|} \right) \quad (G8) \]
\[ S_{\text{inc,inel}}^\text{pow}(Q, \omega) = \sum_j \frac{1}{2} \left( 1 - \frac{\sin(2Q|a_j|)}{2Q|a_j|} \right) \langle \sigma_j(-\omega)\sigma_j(\omega) \rangle \quad (G9) \]
where \( Q = |q| \).
The local correlation function \( \langle \sigma_j(-\omega)\sigma_j(\omega) \rangle \) can be rewritten as a sum over Fourier space, so we have
\[ S_{\text{inc,inel}}(q, \omega) = \sum_{i=1}^8 \sin^2(q \cdot a_i) \sum_{q'} \langle \sigma_i(-q', -\omega)\sigma_i(q', \omega) \rangle \quad (G10) \]
\[ S_{\text{inc,inel}}^\text{pow}(Q, \omega) = \sum_{i=1}^8 \frac{1}{2} \left( 1 - \frac{\sin(2Q|a_j|)}{2Q|a_j|} \right) \sum_{q'} \langle \sigma_i(-q', -\omega)\sigma_i(q', \omega) \rangle \quad (G11) \]
where the sum over \( i \) now runs over the eight sublattices of bonds.

Within the lattice gauge theory description the correlations of the Ising variables \( \sigma \) is directly related to the correlations of the electric field \( E \)
\[ \langle \sigma_i(-q', -\omega)\sigma_i(q', \omega) \rangle = 4 \langle E_i(-q', -\omega)E_i(q', \omega) \rangle \quad (G12) \]
so calculating the correlations of \( E \) in the gauge theory enables us to calculate the incoherent scattering from protons, as shown in Fig. 9. The effects of finite temperature, which lead to the thermal excitation of photons, can also be included, as described in [33].

In Fig. 9, Eq. (G11) is convoluted with a function representing the experimental resolution of the results presented in Ref. [18]. This function is given by the sum of two Gaussians
\[ F_{\text{exp}}(\omega) = A_1 \exp \left( -\frac{\omega^2}{2 \delta_1^2} \right) + A_2 \exp \left( -\frac{\omega^2}{2 \delta_2^2} \right) \quad (G13) \]
where
\[ A_1 = 0.394 \]
\[ \delta_1 = 0.009 \text{ meV} \]
\[ A_2 = 0.006 \]
\[ \delta_2 = 0.037 \text{ meV} \].
