Model selection in neutron Compton scattering - a Bayesian approach with physical constraints

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Abstract. This work analyses the performance of the maximum-likelihood estimation approach in fitting Gram-Charlier expansion curves to nuclear momentum distributions with non-negativity constraints. The presented approach guarantees that the most likely model selected to describe the recorded data is also a physically meaningful one, i.e., corresponds to a non-negative probability distribution function. For the case of the most popular momentum distribution model, containing the information about the variance and excess kurtosis of the distribution, we derive a simple and easy to implement non-negativity criterion. We test the performance of the newly developed approach by applying it to interpret proton momentum distribution obtained from neutron Compton scattering from solid phosphoric acid, a system in which nuclear quantum tunnelling was proposed in the limit of low temperature. From a methodological point of view, this work provides a screening tool in the search for systems exhibiting the so-called 'non-trivial nuclear quantum effects'.

1. Introduction
Neutron Compton scattering (NCS), owing to its unique capability to measure nuclear momentum distributions (NMDs) [1, 2, 3] has been increasingly popular amongst material modelling communities as a benchmarking spectroscopic method-of-choice for a plethora of ab initio methodology, including but not limited to, phonon - lattice dynamics (LD) based on Density Functional Theory (DFT), Born Oppenheimer Molecular Dynamics (BOMD), and Path Integral Molecular Dynamics (PIMD) [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. In practice, however, a hierarchy of approximations, used in treating, analysis and fitting NMD models to NCS data, is confronted with a limited information content that can be extracted from an NCS experiment. More sophisticated NMD models contain a greater number of parameters. Thus, a correspondence naturally establishes itself between the degree of an NMD model sophistication and a level of theory required for the successful modelling of a system under investigation. With the most sophisticated PIMD methodology requiring a lot of computing resources and thus leading to 'heroic simulations' taking months on the most advanced High-Performance Computing (HPC) infrastructure, this benchmarking exercise must be properly optimised.
Thus, a suitable NMD model selection protocol must be established, tested and implemented before one embarks on the materials modelling mission, even with the simplest theoretical tools available. A good example of the need towards establishing such a protocol is the recent NCS work tackling the problem of the phase polymorphism in solid formic acid (FA) [16, 17]. In this work, a series of \textit{ab initio} modelling tools with the systematically increasing level of theory was applied and tested for the agreement with the measured NMD of the proton. LD, BOMD, and the so called quantum-thermostated BOMD (QT-BOMD), making use of the generalised Langevin equation (GLE) [17], were compared. Surprisingly at the first glance, LD-DFT was demonstrated to perform very well, with the QT-BOMD only slightly improving the result [17]. Thus, a preposterous situation arises in which a level of theory requiring at most a day of computing time (LD-DFT) ends up reproducing the experimental result, for all practical intents and purposes, in a same qualitative and quantitative level of agreement, as a 'heroic' QT-BOMD calculation requiring in this case 9 months of HPC time. Moreover, this result fits in very well into a trend, present in the NCS literature, where a simple DFT calculation on an isolated molecule, with additional degrees of freedom (rotational and translational) accounted for in a classical way by resort to the energy equipartition theorem, was able to account very well for the variance of the NMD [18, 19, 9]. The reason behind this lies in the nature of the NCS method. In essence, the second moment of the NMD can be termed as first moment of the atom-projected Vibrational Density of States (apVDOS) [18, 19, 9]. Consequently, its value is most sensitive to the high frequency vibrational excitations chiefly associated with intramolecular vibrations. Thus, as far as the second moment of the NMD is concerned, an isolated-molecule vibrational calculation, using a basic DFT scheme implemented using, e.g., Gaussian software [20], is expected to perform well for molecules in liquids and gases or even condensed matter systems, provided no high-frequency vibrational excitations of inter-atomic nature, with the prominent example of the hydrogen bonding (HB), will be present. Thus, when characterising for instance strongly ionic systems, both solid and liquid, the modelling task can be easily accomplished with a basic molecular DFT level of theory.

Contrary to simple ionic systems, however, systems with HB pose much more challenge from the NMD modelling point of view. Firstly, due to the reasons mentioned above, modelling, even at the level of the second moment of the NMD, will require resorting to LD-DFT methodology, at least. Secondly, when investigating systems with HB at low temperature, nuclear quantum tunnelling (NQT) may show up. In such case, the description of the proton NMD containing the second moment only will not be sufficient. The reason for this is that, protons tunnelling across the HB axis must be described by a coherent superposition of quantum states, naturally leading to bimodal NMDs characterised by non-vanishing excess kurtosis, or even sometimes higher NMD moments [21, 22, 23, 24]. This in turn poses a challenge on both NCS data treatment and modelling fronts. From the data treatment point of view, a model selection protocol is needed to select where to truncate a Gram-Charlier (GC) expansion to describe the observed NMD most accurately but also in a manner which uses only the information present in the data without extending the NMD model overly, not to end up fitting the statistical noise, background or spurious peaks present in recorded NCS data. Motivated by this, a number of Bayesian inference-based model selection protocols for neutron scattering have been established [25, 26, 27, 28, 29], with the recent implementation in the Mantid software, referred to as FABADA, [28, 29]. The second, \textit{ab initio} modelling challenge, is even more formidable. Namely, only one modern \textit{ab initio} modelling approach, the PIMD, is capable of theoretically reproducing NQT in NMD data. With the sophistication and computational cost of the PIMD method sky-rocketing for realistic reproduction of properties of condensed matter systems like quantum liquids or disordered solids, the need for a proper model selection protocol as a gateway to gauge whether PIMD is needed for modelling NMD from NCS data, is rendered even more critical.

Despite the fact that NCS has already witnessed an upsurge of activity in the NMD model
selection and establishment of reliable protocols and software tools [25, 26, 27] one crucial aspect of this exercise has been surprisingly omitted. Namely, the whole NMD model selection so far has boiled down to comparing the likelihood levels of different models without constraining them to be positive from the outset. The figure of merit of the NCS, the NMD, is required by the laws of quantum mechanics to be non-negative, as it can be interpreted as the square of the modulus of a nuclear wave function in the momentum space [1, 2, 3]. Towards this end, NCS experiments allow in principle for the model-free reconstruction of the proton wave function together with its underlying effective Born-Oppenheimer (BO) potential-energy surface of a given nuclide [1, 2, 3]. Mathematically, this reconstruction procedure is reminiscent of the way in which crystal structures are obtained from diffraction data. The presented work is largely motivated by these unique features and capabilities of the NCS method. Its ambition is to establish a model-selection gateway as a guidance for tailored ab initio modelling of nuclear quantum effects, especially in cases where the most quantum of the quantum mechanics phenomena, the quantum coherence, is hoped to be visible in an experiment.

2. Methodology

2.1. Nuclear momentum distributions from neutron Compton scattering

NCS has been described in great detail elsewhere [1, 2, 3]. Here, for the sake of demonstration of basic properties of NMDs, a brief account only will be made of physical assumptions underlying the way NMDs are obtained in the NCS method. The basic setting for the operation of the VESUVIO spectrometer is that it uses electron-volt (eV) neutrons, exclusively provided by spallation sources, such as the ISIS pulsed neutron and muon source in the United Kingdom [30, 31]. Consequently, the energy (E) and momentum (Q), transferred in the scattering process are sufficiently high (in the range 1-100 eV and 30-200 Å⁻¹, respectively) such that the NCS data can be analysed using the so-called impulse approximation (IA), implying that the neutron scatters from a single atomic centre, with conservation of total kinetic energy and linear momentum.

Within the IA, the dynamic structure factor S(Q, E) for a given atom of mass M reduces to a single peak centered at the recoil energy \(E_r = \frac{\hbar^2 Q^2}{2M}\) with \(\hbar = 2.0446\) (meV amu)⁰⁻½ Å [32, 33, 34, 35, 36, 37, 38, 2]. Consequently, \(S(Q, E) = \frac{M}{\hbar^2 Q}J(y)\), where \(y\) is the initial radial momentum \(p\) of the nucleus projected onto the scattering vector \(Q\). \(J(y)\) is the so-called NCS profile [33, 32] and formally corresponds to the longitudinal nuclear momentum distribution (NMD) of the target nucleus along \(y\). In what follows, we will consider the case of harmonically bound isotropic systems (e.g. liquids or crystalline solid powders), constituting the bulk of present-day NCS work on VESUVIO. In this relevant case, a spherically averaged three-dimensional longitudinal NMD, \(J_{1A}(y)\), in the IA limit depends only on the magnitude of \(y\) but not on \(Q\) and can be conveniently expressed via recourse to a Gram-Charlier (GC) expansion of the form [2, 39]

\[
J_{1A}(y) = \exp\left(-\frac{y^2}{2\sigma^2}\right) \sum_n \frac{c_{2n}}{2^{2n}n!} H_{2n}\left(\frac{y}{\sigma\sqrt{2}}\right).
\]  

(1)

where \(H_{2n}\) denotes a Hermite polynomial and the standard deviation (STD) of a given NMD is denoted by \(\sigma\), which, with the present choice of units, is expressed in Å⁻¹. In Eq. (1), the term with \(n = 0\) is set to unity due to the requisite normalization of the NMD. Moreover, with \(c_2\) set to zero, the kinetic energy \(E_k\) of a nucleus of mass \(M\) is related to the STD of its NMD, \(\sigma\), via \(E_k = 3\hbar^2\sigma^2/2M\). This relationship is independent of the precise values of the remaining coefficients \(c_{2n}\). Therefore, the fitting of \(J_{1A}(y)\) to the Gram-Charlier expansion amounts to varying both the width of the momentum distribution \(\sigma\) and the coefficients \(c_{2n}\) with \(n \geq 2\).
For finite values of $Q$, corrections to the IA are known as ‘Final-State Effects’ (FSEs) [38, 2]. To account for FSEs, the method of Sears [32] is routinely incorporated into standard NCS data treatments [38] by expressing the measured NCS profile as a series of the form

$$J(y, Q) = J_{IA}(y) + J_{FSE}(y) = J_{IA}(y) - \frac{M\langle \nabla^2 V \rangle}{36h^2Q} \frac{d^3}{dy^3} J_{IA}(y) + \ldots$$

where $J_{IA}(y)$ is the IA result given by Eq. (1). $\langle \nabla^2 V \rangle$ is the mean value of the Laplacian of the potential energy of the nucleus expressed in meV Å$^{-2}$ (cf. Refs. [38, 40]).

All three Cartesian direction components of the STD of a given NMD, $\sigma_x$, $\sigma_y$, $\sigma_z$, as well as its associated Laplacian of the effective BO potential felt by a nucleus and underlying the NMD under investigation, $\langle \nabla^2 V \rangle$, may be calculated from the underlying apVDOS under the assumption that the FSEs term, given by the Eq. (2) is expressed using the third order Hermite polynomial, $H_3(\frac{\sqrt{Q}}{\sigma\sqrt{2}})$. This results in an expression:

$$J_{IA}(y) = \exp\left(\frac{y^2}{2\sigma^2}\right) \left[ 1 + \frac{c_4}{32} H_4\left(\frac{y}{\sigma\sqrt{2}}\right) - \frac{\sqrt{3}}{12} \frac{\sqrt{Q}}{\sigma^2} H_3\left(\frac{y}{\sigma\sqrt{2}}\right) \right].$$

Additionally, in most of the NCS data treatment protocols used, before the final NMD fit is performed, the FSE contributions are subtracted from data on a detector-by-detector basis in order to separate out the $Q$-dependent terms from the $Q$-independent terms in Eq. (3) [7, 8] (see, Sect. 2.2). Thus in what follows, we will discuss the model selection protocol, based on the Bayesian inference principle, implemented using the FABADA algorithm in Mantid software [28, 29], using the Eq. (3) in the form:

$$J_{IA}(y) = \exp\left(\frac{-y^2}{2\sigma^2}\right) \left[ 1 + \frac{c_4}{32} H_4\left(\frac{y}{\sigma\sqrt{2}}\right) \right].$$

with an additional non-negativity condition imposed, $\forall x \in \mathbb{R}, J_{IA}(x) \geq 0$ with $x$ defined as $x = \left(\frac{y}{\sigma\sqrt{2}}\right)$. This condition is equivalent to a condition involving the Hermite polynomial expansion part of Eq. (4) only:

$$\forall x \in \mathbb{R}, 1 + \frac{c_4}{32} H_4(x) \geq 0.$$ (5)

Moreover, a general connection between $\sigma_x, \sigma_y, \sigma_z$ and the GC expansion coefficients, $c_{2n}$, can be established [43]. In the specific case of the $c_4$ coefficient this relation can be written in the following explicit manner:

$$c_4 = \frac{2}{15} \left( \frac{\sigma_x^4 + \sigma_y^4 + \sigma_z^4}{\sigma^4} - 3 \right).$$ (6)
In what follows, we will analyse which values an NMD based on an underlying multivariate Gaussian distribution may take and how it relates to the above mentioned non-negativity constraints.

2.2. Experimental Protocol

All NCS measurements were performed on the latest incarnation of the VESUVIO spectrometer (see, Fig. 1) at the ISIS pulsed neutron and muon source, United Kingdom [30, 31, 44]. The instrument, both in its operational principles and neutronic parameters, has been extensively described elsewhere [30, 31, 44, 2, 3]. Here, we will only concentrate on the main principles underlying the NMD model selection protocol.

In the vast majority of NCS studies tackling the problem of the visibility in the recorded data of signatures of nuclear quantum coherence, possibly leading to nuclear quantum tunnelling, the studies involve the proton in isotropic condensed matter systems. Due to the conservation of momentum and energy in the Compton scattering within the IA, the NCS scattering off protons, specifically the single scattering process, can occur only for forward scattering angles. Thus, in order to test the newly proposed NMD model selection protocol, we have concentrated in forward scattering NCS data.
The starting point for the analysis of forward scattering NCS data is the expression describing the count rate, \( C_\theta(t) \), of a neutron detector for a scattering angle \( \theta \) in the time-of-flight (t) domain \([2, 3]\):

\[
C_\theta(t) = A' \left[ \frac{E_0 I(E_0)}{Q} \right]_t \sum_{n=1}^{N} I_n M_n J_n[y_n(t)] \otimes R_n[y_n(t)]
\]

(7)

where \( A' \) is a mass-independent experimental constant and the mass-independent factor \([\frac{E_0 I(E_0)}{Q}]_t\) depends on the incident neutron spectrum, \( I[E_0(t)] \), the initial neutron energy, \( E_0(t) \), and the momentum transfer \( Q(t) \), all explicit functions of \( t \). In Eq. (7), the NMD for mass \( M \), \( J_M(y_M(t)) \), is given by Eq. (2) with the expression for the NMD in the IA limit, \( J_{IA}(y) \), given by Eq. (4). Integrated peak intensities \( I_M \) for a given scattering mass \( M \) are proportional to the scattering density \( I_M = AN_M 4\pi b_M^2 \) where \( 4\pi b_M^2 \) is the total (bound) neutron-scattering cross section \([45, 38]\).

The NCS forward scattering data reduction performed in this work follows the literature protocol \([7, 8]\) and can be summarised in few steps:

- raw TOF data were fitted sequentially detector by detector using Eq. (7) in order to obtain the initial values of the fitting coefficients, \( I_M \) and \( \sigma_M \);
- the obtained values of the fitting coefficients, \( I_M \) and \( \sigma_M \) were used as input parameters to calculate the sample-dependent forward scattering corrections: (i) multiple scattering (MS) from the sample and container, and (ii) gamma background (GB) due to cross-talk between signals created at the forward detectors by primary and secondary gold foils (see Figure 1);
- single scattering (SS) raw TOF spectra were generated by subtracting from raw TOF data a linear combination of corrections: (i) MS multiplied by the ratio MS/SS obtained from the measured sample transmission, (ii) GB multiplied by unit factor, and (iii) empty sample container spectrum multiplied by the measured ratio of sample plus container and empty container transmission;
- a second fit to raw TOF data containing SS contributions from different nuclei present in the sample was performed using Eq. (7) and the second iteration of \( I_M \) and \( \sigma_M \) parameter values was obtained. In the second iteration of the fitting algorithm, the values of the \( I_M \) parameters were constrained using the known sample composition (and hence the stoichiometric ratios of numbers of moles of different masses \( M \) present in the sample) and tabulated values of the total (bound) neutron-scattering cross sections \( 4\pi b_M^2 \);
- peaks in the TOF spectra representing neutron recoil of protons (H) were isolated by subtracting, detector by detector, from the raw TOF data corrected in the limit of SS of two independent contributions: (i) the fitting curves of recoil peaks from the other nuclei, and (ii) the fitting curves representing the FSE contributions to NMDs of H/D, given by the term \( \frac{\sqrt{y}}{2} H_3 \left( \frac{y}{\sqrt{2}} \right) \);
- the isolated H recoil peaks were transformed, detector by detector, into respective H longitudinal momentum transfer domains, \( y_H \), a transformation termed as ‘y-space data focusing’. The focused data with greatly improved (by summing 64 spectra) signal-to-noise ratios were finally subject to fitting H NMDs using Eq. (4).

Using the NMD curves obtained after the data pre-treatment steps, described above, model selection was performed using the Bayesian inference tool, FABADA \([28, 29]\). The selection was performed between an NMD model containing purely Gaussian shape, and a model containing a sum of a pure Gaussian term and a Gaussian term multiplied by the Hermite polynomial accounting for non-zero excess kurtosis. Importantly, throughout the whole data reduction, both
in the data pre-treatment steps and in the final analysis of the obtained H NMDs, positivity constraints, given by Eq. (5) were imposed. All data analysis steps were performed within the Mantid software [46, 47, 48, 49].

For the demonstration of the performance of the proposed model selection protocol, a recent example of VESUVIO work, a sample of concentrated, 85wt% phosphoric acid (PA) was chosen. The specimens were enclosed in a 6x6 cm$^2$ flat aluminum (Al) cell resulting in a total transmission of 92% of the sample in the Al container, and 2% transmission level of the empty container, respectively. The data used in the analysis were recorded in the PA solution with the experiment were carried out at 80 K with the sample and container temperature stabilised using a dedicated helium closed-cycle refrigerator.

3. Results and Discussion

3.1. NMD positivity constraint

We begin the description of the non-negativity constrained NMD model selection protocol by noting that the positivity constraint, given by Eq. (5), can be solved analytically in a simple manner by applying a substitution, $x^2 = u$, and thus converting it to a quadratic equation. A quadratic equation with real coefficients can have either one or two distinct real roots, or two distinct complex roots. In this case the discriminant determines the number and nature of the roots. Specifically in our case, if the discriminant is negative, then there are no real roots. Moreover, if the coefficient multiplying the $u^2$ term is positive, the quadratic function is always positive too. Thus, we have:

$$\forall u \epsilon \mathbb{R}, \frac{1}{2} c_4 u^2 - \frac{3}{2} c_4 u + \frac{3}{8} c_4 + 1 \geq 0.$$  \hspace{1cm} (8)

and the equation for the determinant:

$$\Delta = \left(\frac{3}{2} c_4\right)^2 - 2c_4 \left(\frac{3}{8} c_4 + 1\right) = \frac{3}{2} c_4^2 - 2c_4 \leq 0.$$  \hspace{1cm} (9)

With the additional condition that $c_4$ be positive we finally get $c_4(3c_4 - 4) \leq 0$. The final solution for the $c_4$ is then that $0 \leq c_4 \leq \frac{4}{3}$. Thus, any NMD model selection protocol that ensures a non-negative, physically meaningful solution, should include the condition $0 \leq c_4 \leq \frac{4}{3}$ as an additional constraint imposed in fitting.

It is worth noting that, in case of a most general positivity constraint, imposed on a polynomial expansion of the type of the Gram-Charlier series given by Eq. (1), no closed-form analytical solution exists [50] and for each individual series truncated at a different maximal Hermite polynomial order, $n$, the search for specific-case solution is a complicated task, oftentimes motivating special case studies dedicated to finding a solution, mostly using numerical methods [50]. Interestingly for our specific case, a study exists in the literature by Jondeau and Rockinger [50] concerning a positivity constraint for a GC expansion of the type $\forall x \epsilon \mathbb{R}, 1 + cH_4(x) + kH_3(x) \geq 0$. Using sophisticated methods of analytical geometry and numerical analysis, the authors have found a region in parameters space of the excess kurtosis, $c$, and skewness, $k$, that corresponds to a positive solution (see Figure 2 taken from Ref. [50]). Importantly, this region is not rectangular in shape which has an important consequence that for any pair of parameters $(c,k)$ giving a positive solution, one of them is not independent on the other.

Interestingly, a specific solution within the class given by Jondeau and Rockinger exists for the case of vanishing skewness of the distribution. This corresponds to the zero value abscissa in Figure 2 from Ref. [50]. The zero-skewness abscissa defining a positive GC expansion value region is bounded from below by zero and from above by a value of 4. Using the definition of
Figure 2. Feasible region of excess kurtosis, $c$, and skewness, $s$, defining the parameter region for which positive GC expansion values exist together with a maximum likelihood estimator (denoted by a filled circle symbol), taken from Jondeau and Rockinger, Ref. [50].

The excess kurtosis, $c = \frac{M_4}{\sigma^4} - 3$, with $M_4$ being the fourth moment of the distribution, defined as, $M_4 = 3(1 + c_4)\sigma^4$, we get $c = 3c_4$ and $0 \leq 3c_4 \leq 4$. Thus, the specific case of the solution given by Jondeau and Rockinger coincides with our solution given above based on the simple consideration of a quadratic equation.

Beyond the special, albeit very popular in the NCS literature, case of the zero-skewness NMD models containing the Gaussian term and the term with excess kurtosis only, one is tempted to formulate a more general NMD positivity criterion beyond this special, relatively simple case. A first step in that direction is to consider an NMD of a type given by Jondeau and Rockinger, i.e. with non-zero skewness. Here, already a first difficulty arises. Namely, the solution given by Jondeau and Rockinger cannot be directly employed as a positivity constraint in NCS as the skewness parameter they consider is independent on an external variable, like the magnitude of the momentum transfer $Q$ in NCS. In case of NCS the problem is even more complicated.
as, due to the kinematics of momentum and energy conservation within the limits of the IA, \( Q \) depends in a parametric manner on the TOF, differently for scattering angle \( \theta \). This is exactly the case why, in the NCS data pre-treatment protocol described above, the FSE subtraction is performed before the NCS data for the isolated recoil peak is focused in its \( y \)-space and fitted with an NMD model. At present, the non-negativity constraint is not explicitly imposed at the pre-treatment stage. All fitting curves, obtained in a detector-by-detector manner, are simply visually inspected and raw spectra yielding negative solutions in fitting are simply pruned out and excluded from the final selection of spectra for the focusing and final NMD fit. Work is in progress, within the joint effort of the Mantid software development team, to implement a general positivity constraint for any Gram Charlier series truncation scheme, both at the pre-fit (with different detector-grouping schemes) and final NMD fit stage, using numerical methods employing Chebychev polynomial expansion.

3.2. Multivariate Gaussian NMD and the positivity constraint

A second very popular NMD model, exploited extensively beside the GC expansions to describe nuclear chemical dynamics in liquids and solids within the harmonic approximation, is the model in which NMDs are described using a multivariate Gaussian (MVG) [2, 3]:

\[
J_{\text{MVG}}(y) = \frac{1}{\sqrt{8\pi^3\sigma_x^2\sigma_y^2\sigma_z^2}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \exp\left(-\frac{y^2}{2\sigma_z^2}\right) \Omega
\]

where \( \Omega \) denotes the angular average. It is thus of importance to establish mathematical connection between the MVG and GC expansions, especially in the light of the positivity constraint discussed in Section 3.1. In this work, we will concentrate only on the MVG connection to the truncated GC expansion considered above by noting first that, the connection between the two GC parameters, \( \sigma \) and \( c_4 \) has already been given above (see, Eq. (6)).

For the specific form of the \( c_4 \) coefficient, given by Eq. (6), one may inspect the connection by plotting the values of \( c_4 \) as a function of \( \sigma_x, \sigma_y, \) and \( \sigma_z \) in a relevant range of those MVG second moment values. Such a plot is shown in Figure 3.

Already a first glance at the Figure 3 reveals that, \( c_4 \) values, plotted within a cube of values of the \((\sigma_x, \sigma_y, \sigma_z)\) parameters of the MVG model ranging from 0 to 50 Å\(^{-1}\), seems to be bounded from below by the zero value and from above by the value of 0.8. Indeed, a further function maximum search using an unconstrained optimisation scheme by means of the \texttt{fminsearch} algorithm, implemented in Matlab 2017a software [51], reveals that the function is constrained in the region 0–0.8, with the maximum of 0.8 obtained always for the solution having the symmetry, \( \sigma_i = \sigma_j = 0, \sigma_k > 0 \). Within the domain plotted in Figure 3 the non-linear optimisation algorithm finds two maxima, \( c_4 = 0.8 \) at \((0, 0, 23.245)\) and \((0, 0, 49.6)\).

A special, albeit very important and popular in the literature [2, 3, 18] case exists when two of the three values of the second moment of the MVG become identical, by virtue of the symmetry of the NMD, i.e. \( \sigma_x = \sigma_y = \sigma_t \). In this special case, \( c_4 = \frac{4}{15} \left( \frac{\sigma_t^2 - \sigma_z^2}{\sigma_t^2} \right)^2 \) with \( \sigma^2 = \frac{2\sigma_t^2 + \sigma_z^2}{3} \) [24]. The plot of the \( c_4 \) as a function of \( \sigma_t \) and \( \sigma_z \) is shown in Figure 4.

In this important case, the MVG becomes a relatively simple two dimensional function and its properties can be investigated using simple methods of mathematical analysis. Specifically, it can be proven that the \( c_4 \) function in this case does not have a proper minimum nor a maximum. Instead, \( c_4 \) attains a minimal value at \( \sigma_t, \sigma_z = 0, 0 \) which is a saddle point. Moreover, \( c_4 \) reaches its maximal value, \( c_4 = 0.8 \), asymptotically as a limit \( \sigma_t = 0, \sigma_z \rightarrow \infty \). At another important case, \( \sigma_z = 0, \sigma_t \rightarrow \infty \), the function reaches its second limit \( c_4 = 0.2 \).

On the whole, the main conclusion from the analysis of the MVG connection to the GC expansion of the NMD is that, any sensible choice of values of the second moment of the MVG will always lead to an NMD which, when expanded in the GC expansion containing only the...
Figure 3. Values of $c_4$, given by Eq. (6), as a function of $\sigma_x$, $\sigma_y$, and $\sigma_z$. See text for details.

Gaussian term and the terms responsible for non-vanishing excess kurtosis, will always lead to values of $c_4$ bounded from below by zero and from above by the value of 0.8.

Moreover, this result has another very important consequence for screening the NMDs obtained from NCS experiments for the signs of coherence of a nuclear wave packet and thus possibly nuclear quantum tunnelling. Namely, when a GC expansion fit of the type discussed here, performed on an experimentally obtained NMD form a NQT-candidate NCS data, converges with a $c_4$ value above 0.8 (taking into account the error bar on the value of $c_4$), a conclusion must be reached that the underlying BO effective potential cannot correspond to an MVG distribution. In other words, no three-dimensional harmonic potential, leading to an MVG NMD can possibly yield, in a GC expansion, $c_4$ values above 0.8. This condition is, however, only a necessary but not a sufficient one, i.e., bi-modal BO effective potentials of a type of a double-well, which naturally lead to solutions of nuclear Schroedinger equations exhibiting nuclear quantum coherence across both wells, may still have $c_4$ values below 0.8. For instance, in a study comparing proton NMDs in liquid water, ice, supercritical water, and water under pressure confined in C60, Reiter et al. [24] fitted an NMD model in which, in a frame of reference where an individual bond is taken to lie along the z axis, the motion transverse to the bond is harmonic and along the bond given by a distribution that corresponds in real space to two Gaussians separated by a distance $d$. The fitting of this model leads to a result that values of the excess kurtosis above ca 0.3 (with the values of the coefficient $c_6$ vanishing within the experimental error) are associated with a bimodal proton wave function across the hydrogen bond with the two maxima separated by ca 0.3 Å. For the values of $c_4$ below ca 0.3 and values of $c_6$ equal to zero to within the experimental accuracy the model leads to a wave function which is a single modal bivariate Gaussian ($d = 0$). Thus, within the model by Reiter et al., the values of $c_4$ above 0.8 will certainly always lead to a double-well effective BO potential with nuclear
quantum coherent wave packet as a solution, albeit values of $c_4$ above ca 0.3 and still below 0.8 already start producing such solutions.

3.3. Bayesian inference with positivity constraint in action: experimental NMD study of an NQT-candidate structure

In order to demonstrate the performance of the Bayesian-inference principle with positivity constraints in fitting NMDs from an NCS experiment, we show here an example from a recent VESUVIO work [52]: a proton NMD obtained from an NCS experiment on frozen disordered concentrated (85 wt%) solution of the phosphoric acid (PA) at $T=80K$. The following protocol was adopted. The FABADA tool, implemented in Mantid software [46, 47, 48, 49] was employed to compare four models: (i) a model with purely Gaussian NMD; (ii) a model with a sum of two terms, a Gaussian and a Gaussian multiplied by the excess kurtosis term in the GC expansion without positivity constraints, (iii) the same model with positivity constraints imposed in fitting, (iv) a model with a Gaussian term, the excess kurtosis term and an additional term proportional to $c_6 H_6(x)$ without positivity constraints imposed in fitting.

The result of the NMD model selection protocol for the proton NMD obtained from NCS data recorded from the PA sample is illustrated in Figure 5. The first observation is that, to within the
Figure 5. The result of the NMD model selection protocol for the proton NMD obtained from NCS data recorded from frozen disordered concentrated (85 wt%) PA solution at T=80K. (i) green line – a model with purely Gaussian NMD; (ii) red line – a model with a sum of two terms, a Gaussian and a Gaussian multiplied by the excess kurtosis term in the GC expansion without positivity constraints, (iii) blue line – the same model with positivity constraints imposed in fitting, (iv) black line – a model with a Gaussian term, the excess kurtosis term and an additional term proportional to $c_6 H_6(x)$ without positivity constraints imposed in fitting. See text for details.

Experimental accuracy, a model with a sum of two terms, a Gaussian and a Gaussian multiplied by the excess kurtosis term in the GC expansion, yields the same probability distribution function (PDF) no matter the positivity constraints are applied or not. Moreover, in both cases the the values of the most likely parameters, $c_4$ and $\sigma$, are identical to within the experimental error and yield, $0.84 \pm 0.07$ and $6.7 \pm 0.2 \text{ Å}^{-1}$ respectively. The proton NMD curve fitted to experimental data using this model is shown in Figure 6. The inset shows the polynomial part of the GC expansion plotted for the optimal $c_4$ values of 0.84 ± 0.07. It clearly shows that the solution is positive for all values of the reduced variable $x$, as predicted by the positivity constraint condition developed in this work. Importantly, in the context of the NQT, the solution provided by this model strongly suggests the existence of the coherent supersposition of the proton wave.
Figure 6. Main: The proton NMD curve fitted to experimental data recorded from frozen disordered concentrated (85 wt%) PA solution at T=80K. The model used involves an NMD containing a sum of two terms, a Gaussian and a Gaussian multiplied by the excess kurtosis term in the GC expansion with positivity constraints: the raw data is shown in black, the best fit NMD curve is reported light blue together with the instrument resolution function for protons in navy blue. The convolution of the NMD curve with the resolution function, which was subject to direct fitting to the experimental data, is shown as red trace and the fit residual is shown in green. Inset: the polynomial part of the GC expansion plotted for the optimal $c_4$ values of $0.84 \pm 0.07$. See text for details.

packet in the PA system under investigation, which may mark the onset of the temperature regime at which tunneling may be possible of protons across the HBs in the PA. It is worth noting that, mathematically similar solution, i.e. $c_4=0.720 \pm 0.158$, was found by Reiter et al. in fitting a GC to NCS data recorded in KH$_2$PO$_4$ (KDP) at T=90K and taken as a sign of the coherence over two locations for the proton observed in the paraelectric phase. [23]

The second observation is that the Bayesian inference prefers the model with a Gaussian term, the excess kurtosis term and an additional term proportional to $c_6 H_6(x)$. However, without any positivity constraints imposed on this model in fitting FABADA minimiser converges to a non-
positive solution, as evidenced by the polynomial part of the GC expansion plotted for the optimal $c_4$ and $c_6$ values found, i.e. $0.605 \pm 0.06$ and $-0.6 \pm 0.1$, respectively, as shown in the inset of Figure 7.

Two important ramifications emerge from the case study illustrated in Figure 7. First of all, unlike suggested by Jondeau and Rockinger [50], the maximum likelihood estimation does not naturally find a solution which is a non-negative GC expansion (as denoted by the closed circle symbol in Figure 2). At least, it does not seem to be an inherent feature of this type of the estimation. Secondly, drawing from the example of the solution for the GC expansion containing the skewness and excess kurtosis terms by Jondeau and Rockinger [50], we can already say at this point that a general solution most likely will contain a high degree of correlation between the $c_4$ and $c_6$ values. The shape of the region in $(c_4, c_6)$ parameter space may, in general, be very complicated, most likely to be found by a numerical solution. Moreover, an analytical solution that would describe the $c_4 - c_6$ correlation, even if it exists, would be very difficult to implement in fitting software.

An important realisation from the analysis of the performance of the positivity constraint implementation in the Bayesian NMD model selection, as applied to NMD data from the NCS experiment described above, is that the unconstrained solutions lead to NMD curves with negative values far away from the peak centre, in the regions of the longitudinal momentum distributions which oftentimes escape the scrutiny of the NCS data analysis. However, it is important to note in that respect that the mere fact that a numerical solution of the fitting of a given NMD model adopts positive values only in the kinematic domain accessible by the instrument does not signify that the obtained solution is physically meaningful. Owing to the unique nature of NCS, it is a basic postulate of quantum mechanics, namely the Born interpretation linking the square of the wave function to the probability distribution in the whole domain of the parameters on which this function depends, that intervenes here and provides a much-sought physical meaningfulness criterion.

4. Outlook
In this work we have presented a much-needed case study of the implementation of the NMD model ranking protocol, based on Bayesian inference with additional NMD positivity constraints. The protocol ensures that the NMD solutions obtained from the NCS data analysis are physically meaningful. Moreover, owing to the mass-selective nature of the NCS technique [53, 54, 55, 3, 56], this criterion can be implemented for NMDs of all masses in a given system under investigation, which strengthens the protocol performance in pruning out unphysical solutions from the investigation of any molecular and condensed matter nuclear quantum tunnelling-candidate systems.

The results presented herein provide a suitable platform for a future development of a robust and easy to implement NCS data screening procedure that would constitute the first crucial step in the understanding of nuclear quantum effects, a prerequisite for a suitable choice of the level of $ab$ initio theory employed for system modelling. The ultimate goal to this end is the development of a hierarchy of the applicability of subsequent $ab$ initio theory levels and their practical implementations in the quantum chemistry software that would match the degree of the information about the nuclear quantum effects present in the recorded NCS data, as categorised by Bayesian inference. In this way, 'heroic quantum simulations' would be proposed and applied to the characterisation of only those NCS data sets that would positively pass the Bayesian screening protocol. Conversely, systems exhibiting no marked 'non-trivial' nuclear quantum effects (e.g. no signatures of tunnelling in the NCS data) could be tackled by relatively low-cost lattice dynamics DFT-based methods. The overarching goal of the strategy described in this work is to further increase the level of much-needed synergy between NCS experiments and computational materials modelling.
Figure 7. Main: The proton NMD curve fitted to experimental data recorded from frozen disordered concentrated (85 wt%) PA solution at T=80K. The model used involves a Gaussian term, the excess kurtosis term and an additional term proportional to $c_6 H_6(x)$ without positivity constraints imposed in fitting: the raw data is shown in black, the best fit NMD curve is reported light blue together with the instrument resolution function for protons in navy blue. The convolution of the NMD curve with the resolution function, which was subject to direct fitting to the experimental data, is shown as red trace and the fit residual is shown in green. Inset: the polynomial part of the GC expansion plotted for the optimal $c_4, c_6$ values of 0.605 ± 0.06, -0.6 ± 0.1 respectively. See text for details.
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