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Attosecond protonic 'Schrödinger's cat' states and anomalous neutron scattering

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Abstract

Recent neutron Compton scattering (NCS) investigations on niobium, palladium and yttrium hydrides at ambient temperatures revealed a striking anomalous behaviour of the total neutron scattering cross-section densities of protons, in the sub-femtosecond time scale. These experiments were motivated by: (i) our previous theoretical work on short-lived quantum entanglement (QE) of protons in condensed matter, and (ii) our first experimental verification of this effect with NCS from liquid H_2O/D_2O mixtures. Based on elementary and/or basic results of neutron scattering theory, and incorporating the effects of QE and decoherence into the formalism, a first-principles theoretical interpretation of this novel effect is provided.

Keywords: Metallic hydrides; Neutron Compton scattering; Protons; Quantum entanglement; Decoherence; Attosecond dynamics

1. Introduction

The counter-intuitive phenomenon of quantum entanglement (QE) between two or more quantum systems has emerged as the most emblematic feature of quantum mechanics [1]. Entangled states are often called Schrödinger's cat states. Experiments investigating QE, however, are focussed on a collection of a small number of simple (two- or three-level) quantum systems thoroughly isolated from their environment (e.g. atoms in high-Q cavities and optical lattices, or trapped ions), or coupled to it by well-known and controlled interaction mechanisms. These experimental conditions are necessary due to the decoherence [2,3] of quantum systems. In short, the process of decoherence refers to the suppression of quantum superpositions caused by interactions of the system with the environment.

By contrast, QE in condensed and/or molecular matter at ambient conditions is usually considered to be experimentally inaccessible, due to the very fast and extremely effective, decoherence. However, our previous theoretical investigations [4] concerning a novel short-lived QE of protons (or H-atoms) in condensed systems have proposed to confirm this effect experimentally by applying sufficiently 'fast' scattering techniques, like neutron Compton scattering (NCS). Furthermore, in 1995 we detected for the first time this new quantum effect on water [5–7]. After that, various systems have been investigated, e.g. metallic hydrides (in collaboration with E. Karlsson) [8–10], polymers [11,12], liquid benzene [12], and amphiphilic molecules [13]. All NCS experiments were carried out with the electron-volt spectrometer (eVS) of ISIS (Rutherford–Appleton Laboratory, UK), which is presently the world's most powerful pulsed spallation neutron source.

All these NCS experiments provided direct evidence for the predicted QE of protons in the sub-femtosecond (i.e. attosecond) regime. The most striking result has been that the measured neutron scattering intensity from protons exhibits a very strong 'anomalous' decrease, in some cases even by ≈30%. This surprising result may be illustrated by saying that some protons seem to exhibit a new kind of short-time 'destructive interference'. It has been emphasized that this effect has no conventional (classical or quantal) interpretation [14].

Here, considering our NCS experiments on metallic hydrides and also extending previous investigations [11], we provide a concise theoretical interpretation of this effect, which is based on the well-established neutron

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scattering formalism (see, for example, the excellent textbook of Squires [15]) and incorporates basic elements of QE and decoherence theory [2,3].

2. Connection with NCS experiments

We have investigated with NCS the considered QE effect from niobium [8], palladium [9] and yttrium [10] hydrides with various H and D contents. All these experiments have clearly confirmed the existence of this effect. Most recently, preliminary experiments with the well-known ZrH_2 system have also been successful.

It is important to note that the scattering time τ_{sc}, i.e. the interaction time of the (epithermal) neutrons with the struck nuclei, of NCS is very short, being in the sub-femtosecond time scale [6,8,11]. This is a consequence of the large energy and momentum transfers (for the neutron–proton collision): $\Delta E \approx 3-150$ eV and $q=|\mathbf{q}| \sim 10-120$ Å^{-1}. Consequently, the recoil peaks of protons, deuterons, and some other heavier nuclei can be resolved in the measured time-of-flight (TOF) spectra. This fact is crucial for the precision and reliability of our experiments because it makes possible the direct determination of the ratio A_H/A_X of the areas under the recoil peaks of H and X (with X=Nb, Pd, etc.). According to well-established theory, under the prevalent conditions of our NCS experiments, the equation:

$$A_H/A_X = N_H\sigma_H/N_X\sigma_X \tag{1}$$

must be strictly valid [6]. N_H/N_X is the ratio of the particle number densities of H and X, which is precisely known through sample preparation. σ_H and σ_X are the total neutron scattering cross sections of H and another atom X. Thus, since the conventionally expected values of σ_H and σ_X are given in standard tables [16], the validity of Eq. (1) is immediately subject to experimental test.

For a description of the eVS instrumental setup and the data analysis procedure, see Ref. [11].

All the aforementioned experimental results reveal that the basic Eq. (1) is strongly violated: usually, the measured ratio A_H/A_X appears to be 'anomalously' reduced by 15–40%. This striking effect has been attributed to protonic QE (also involving 'dressing' with electronic degrees of freedom), which, due to the very fast and effective decoherence process, is very short-lived in condensed matter (see Refs. [11–13,17]).

3. Theoretical interpretation

In this section, a concise (and self-contained) theoretical interpretation of the 'anomalous' NCS effect under consideration is presented. The starting point is given by some elementary results of standard theory of neutron scattering, and their specialization to the context of large momentum transfer. The corresponding notations and derivations are following the presentation of Squires [15].

Let us temporarily assume (for simplicity of notations) that the condensed system consists of N atoms of the same kind only. The usual starting point is to consider the number of neutrons $\mathrm{d}I_{sc}/\mathrm{d}E_1$ scattered per second into a small solid angle $\mathrm{d}\Omega$ (in some given direction) with final energy between E_1 and $E_1+\mathrm{d}E_1$:

$$\frac{\mathrm{d}I_{sc}}{\mathrm{d}E_1} \sim \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E_1} \tag{2}$$

i.e. it is proportional to the double differential cross section of the system:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E_1} = \frac{k_1}{k_0}\sum_{\nu\nu'} W_\nu \left| \sum_j b_j \langle \nu' | \exp(i\mathbf{q}\cdot\mathbf{r}_j) | \nu \rangle \right|^2 \delta(E_\nu - E_{\nu'} + E_0 - E_1) \tag{3}$$

b_j is the so-called 'bound' scattering length [15] of atom j ($=1,\ldots,N$) and $|\mathbf{k}|_i = k_i$. $\hbar\mathbf{q}$ and $\hbar\omega$ are the momentum and energy transfers from the neutron to a struck nucleus; i.e, $\hbar\mathbf{q} = \hbar\mathbf{k}_0 - \hbar\mathbf{k}_1$, $\hbar\omega = E_0 - E_1$. The subscripts '0' and '1' refer to neutron quantities 'before' and 'after' collision, respectively. Accordingly, ν and ν' refer to the initial and final state of the scattering system, respectively, i.e. the transition $|\nu\rangle \to |\nu'\rangle$. Usually, the many-body states $|\nu\rangle$ and $|\nu'\rangle$ are assumed to be eigenstates of the many-body Hamiltonian H, and W_ν represent Boltzmann probabilities. The first Born approximation (being equivalent to Fermi's golden rule) is valid here, and as a consequence the cross section depends only on the changes in energy and wave vector of the neutron. The potential describing the neutron–nucleus interaction is Fermi's pseudopotential [15].

As is demonstrated in textbooks of neutron scattering theory, the general expression Eq. (3) applies to all neutron scattering techniques and is valid very generally. In particular, it also holds in such specific cases in which correlations between spatial co-ordinates and b-values of pairs of nuclei do exist, for example, when *quantum exchange correlations* are significant, as e.g. in the case of ortho- and para-hydrogen [15]. Furthermore, Eq. (3) can describe scattering by (any given number of) particles exhibiting no spin entanglement, but spatial QE only.

In the experiments revealing the 'anomalous' effect mentioned above, the energy resolution plays a minor role, and thus it suffices to consider the differential cross section:

$$I_{sc}(\mathbf{q}) \sim \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \int_0^\infty \mathrm{d}E_1 \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E_1} \right) \sim \frac{k_1}{k_0}\sum_{\nu\nu'} W_\nu \left| \sum_j b_j \langle \nu' | \exp(i\mathbf{q}\cdot\mathbf{r}_j) | \nu \rangle \right|^2 \tag{4}$$

Here we use the following property of the Dirac delta function: $\int \delta(a-x)\,dx = 1$.

In the last equation, the sum Σ_j contains N terms. So the square of its absolute value, $|\Sigma_j|^2$, is the sum of N^2 terms of which a typical member is:

$$\begin{aligned} M_{jj'\nu\nu'} &\equiv b_j b_{j'} \langle \nu' | \exp(i\mathbf{q}\cdot\mathbf{r}_j) | \nu \rangle \langle \nu | \exp(-i\mathbf{q}\cdot\mathbf{r}_{j'}) | \nu' \rangle \\ &= b_j b_{j'} Tr\big[\, \rho_{\nu'} \otimes \exp(i\mathbf{q}\cdot\mathbf{r}_j) | \nu \rangle \langle \nu | \exp(-\,i\mathbf{q}\cdot\mathbf{r}_{j'}) \big] \\ &\equiv b_j b_{j'} Tr\big[\, \rho_{\nu'} \otimes | \mathscr{E}_{\nu j} \rangle \langle \mathscr{E}_{\nu j'} | \big] \end{aligned} \tag{5}$$

where the definition $|\mathscr{E}_{\nu j}\rangle \equiv \exp(i\mathbf{q}\cdot\mathbf{r}_j)|\nu\rangle$ is introduced for the sake of brevity of the following derivations. Here, the scattering length is assumed to be real, $\rho_{\nu'} \equiv |\nu'\rangle\langle\nu'|$ is the exact density operator corresponding to the *final* state ν', and $Tr[\ldots]$ denotes the trace operation with respect to all degrees of freedom. $\rho_{\nu'}$ is introduced for reasons which will become apparent below.

Being of particular importance for our NCS investigations, we now consider exclusively the physical case of *high momentum transfer*, i.e $|\mathbf{q}| \gg 2\pi/d$; d is the nearest-neighbor distance of two scattering nuclei. As a consequence, the spatial scale of the scattering event, represented by $1/q$ (where $q = |\mathbf{q}|$), is too small for one to detect interference effects due to scattering from pairs of different nuclei; see the right-hand site (rhs) of Eqs. (4) and (5). This happens because the terms with $j \neq j'$ in this equation correspond to fine—spatially oscillating, i.e. constructive and destructive—interference patterns which tend to average to zero due to the finite spatial (and solid angle) resolution of the detector (for illustration, see Figs. 1–5 of the 'Feynman Lectures' [18]).

These physical considerations imply that the terms with $j \neq j'$ do not contribute to the measured scattering intensity, and therefore one obtains from Eq. (5):

$$M_{jj\nu\nu'} = b_j^2\, Tr\big[\, \rho_{\nu'} \otimes | \mathscr{E}_{\nu j} \rangle \langle \mathscr{E}_{\nu j} | \big] \tag{6}$$

This limit is usually termed 'incoherent approximation' [19]. It should be emphasized that, according to the preceding reason, the distinct terms with $j \neq j'$ have not just been 'neglected' in this equation. Furthermore, since the above equations follow straightforwardly from Eq. (3) in the limit $q \gg 2\pi/d$, they also apply to the case of systems exhibiting quantum exchange correlations, the latter being still included in the properly chosen many-body quantum states $|\nu\rangle$ and $|\nu'\rangle$.

For our purposes, however, the main result of the preceding derivations concerns the interpretation of the effect of 'anomalous' reduction of scattering intensity (see Section 1). Since the quantity $|\mathscr{E}_{\nu j}\rangle\langle\mathscr{E}_{\nu j}|$ is a projector (thus having eigenvalues 0 or 1) and $\rho_{\nu'}$ is a density operator (thus having non-negative eigenvalues), the product of the two operators must be hermitian and positive semidefinite. Consequently:

$$Tr\big[\, \rho_{\nu'} \otimes | \mathscr{E}_{\nu j} \rangle \langle \mathscr{E}_{\nu j} | \big] \geq 0 \quad \text{and} \quad M_{jj\nu\nu'} \geq 0 \tag{7}$$

Thus, in the expression of the scattering intensity:

$$I_{sc}(\mathbf{q}) \sim \frac{d\sigma}{d\Omega} \sim \frac{k_1}{k_0} N\overline{b^2} \sum_{\nu\nu'} W_\nu Tr\big[\, \rho_{\nu'} \otimes | \mathscr{E}_\nu \rangle \langle \mathscr{E}_\nu | \big] \tag{8}$$

occur now only non-negative terms. On the last equation, the average $\overline{b^2}$ over all N identical particles is introduced, and the subscript j has been dropped since it is immaterial here. As the cross-section is given by $\sigma = 4\pi b^2$, the last result implies $I_{sc} \sim N\sigma$, which is tantamount to the basic Eq. (1).

To proceed, recall that the excited pure state $\rho_{\nu'}$ refers to the complete (many-body) system. Due to the smallness of $1/q$ (see above), the neutron–nucleus scattering process itself concerns only a much smaller number of 'relevant' degrees of freedom. Thus, in Eq. (8) it is sufficient to use the reduced density operator $\rho^r_{\nu'}$ obtained from $\rho_{\nu'}$ through partial trace $Tr_{(\mathrm{env})}$ over the 'remaining' degrees of freedom (often termed 'environment'):

$$\rho^r_{\nu'} = Tr_{(\mathrm{env})}[\rho_{\nu'}] = Tr_{(\mathrm{env})}[|\nu'\rangle\langle\nu'|] \tag{9}$$

Thus, a typical member of the sum in Eq. (8) contains the quantity:

$$m_{\nu\nu'} \equiv Tr\big[\, \rho_{\nu'} \otimes | \mathscr{E}_\nu \rangle \langle \mathscr{E}_\nu | \big] = Tr\big[\rho^r_{\nu'} \otimes | \mathscr{E}_\nu \rangle \langle \mathscr{E}_\nu | \big] \tag{10}$$

These results are valid for systems being composed of non-entangled particles at all, as well as for those exhibiting (any degree of) quantum entanglement.

Let us now consider the quantity (10), which is suitable for the study of the consequences of *decoherence*. First, note that the highly excited state $\rho^r_{\nu'}$ is far from equilibrium and thus may be subject to decoherence (One may consider this physical assumption to be our 'working hypothesis'). Of particular interest for our work is the fact that the dynamics of a scattering system may be properly described in a *preferred representation* (sometimes also called *pointer basis*), related with the set of state vectors $\{|\xi\rangle\}$ in which the phenomenon of decoherence appears (Being a basis, this set contains excited as well as initial states). According to present-day knowledge, the preferred representation of any open quantum system is not arbitrary, but selected by the quantum dynamics of the system. This interesting point has been particularly emphasized by Zurek [3]. According to decoherence theory, the dynamics of $\rho^r_{\nu'}$ in the preferred representation reads [2,3,11]:

$$\langle \xi | \rho^r_{\nu'}(t) | \xi' \rangle \equiv \langle \xi | \rho^r_{\nu'}(0) | \xi' \rangle\, e^{-\Lambda|\xi-\xi'|^2 t} \tag{11}$$

Performing the trace in Eq. (10) with respect to the basis $\{|\xi\rangle\}$ and noting the closure relation $\int d\xi' |\xi'\rangle\langle\xi'| = \hat{\mathbf{1}}$, Eq. (10) may be written as:

$$\begin{aligned} m_{\nu\nu'}(t) = \int\!\!\int d\xi\, d\xi'\, \langle \xi | \rho^r_{\nu'}(0) | \xi' \rangle \langle \xi' | \mathscr{E}_{\nu j} \rangle \\ \langle \mathscr{E}_{\nu j} | \xi \rangle\, e^{-\Lambda|\xi-\xi'|^2 t} \end{aligned} \tag{12}$$

This quantity contains a t-dependence due to the decoherence effect, the latter being related with the non-diagonal elements of the reduced (or: relevant) density operator (Eq. (11)). Obviously, time-resolved details of this (very fast) time dependence are not accessible to any neutron scattering experiment. Therefore, comparison with experimental results should be made after taking the time average over the duration of the scattering process, given by the scattering time τ_{sc}. Thus, the associated experimentally relevant quantity is:

$$\overline{m}_{\nu\nu'} \equiv \frac{1}{\tau_{sc}} \int_0^{\tau_{sc}} \mathrm{d}t\, m_{\nu\nu'}(t) \qquad (13)$$

From relations (7) it also follows $m_{\nu\nu'}(t) \geq 0$ and $\overline{m}_{\nu\nu'} \geq 0$.

Furthermore, the presence of decoherence implies that all terms contributing to I_{sc} are reduced due to the decaying exponential factors $\exp(-\Lambda|\xi - \xi'|^2 t) \leq 1$. That is, from Eq. (8) we obtain:

$$I_{sc} \sim \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \sim \frac{k_1}{k_0} N\overline{b^2} \sum_{\nu\nu'} W_\nu \overline{m}_{\nu\nu'} \qquad (14)$$

where all terms in the sum are nonnegative. This result implies immediately that the t-decaying exponential factors cause always a reduction of any term contributing to the scattering intensity I_{sc}—as compared to the associated term for the case of no decoherence (i.e. $\Lambda = 0$). In short:

$$I_{sc}[\Lambda \neq 0] < I_{sc}[\Lambda = 0] \qquad (15)$$

This provides the interpretation of the considered 'anomalous' effect.

4. Discussion

Due to decoherence, the considered QE effect cannot be observed with 'very slow' techniques (corresponding to the limit $\tau_{dec} \ll \tau_{sc}$), like, for example, neutron interferometry [20]. This is also in agreement with the theoretical results of Ref. [17], which considers exchange correlations to be the dominant cause of our effect, but in which decoherence plays no explicit role. QE effects between pairs of adjacent protons have been shown to strongly affect the proton transfer and/or vibrational dynamics in the molecular crystal $KHCO_3$, in particular applying the method of incoherent elastic neutron scattering [21].

In contrast to Ref. [17], exchange correlations represent no necessary condition for our theory. In order to test the physical relevance of this crucial point, we are currently investigating the NCS spectra of isotopically mixed molecular hydrogen HD (which cannot exhibit exchange correlations) and compare then with those of H_2. The existing preliminary results [22] show that both these systems exhibit the same 'anomaly', thus refuting the alleged 'dominant role' of exchange correlations.

The above derivations lead to the conclusion that the QE effect may become observable in a suitable 'decoherence time window' only, viz. when $\tau_{dec} \sim \tau_{sc}$. In the limiting case $\tau_{dec} \gg \tau_{scatt}$, our results predict that no 'anomaly' will exist.

The presented results strongly affect the conventional and widely used theoretical concept of electronic Born–Oppenheimer (BO) energy surfaces. Recall that BO surfaces are determined by considering the nuclei as classical mass points and fixing them at various spatial configurations, which allows then to solve the associated 'electronic' Schrödinger equations. As a matter of fact, our results clearly demonstrate that the protons in metallic hydrides (and other systems) cannot be described as classical mass points in the sub-femtosecond time scale. This conclusion may also have considerable multidisciplinary implications, since this time scale is of the order of the characteristic time of the electronic rearrangements accompanying: (i) the formation and/or breaking of a typical chemical bond in a molecule, or (ii) certain changes of positions of protons in a metallic lattice.

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