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Quantum coherence of protons in metal hydrides

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Abstract

Single protons can be found in tunneling states in certain metal hydrides. Similar situations can also be observed for implanted positive muons. The basic features of such states and conditions for their existence will be reviewed. The quantum coherence is easily destroyed by decoherence mechanisms related to the coupling of the protonic states to phonons and conduction electrons.

Similarly, pairs or small clusters of protons in metal hydrides have been shown to be quantum correlated when observed over very short time-scales with neutron techniques. This two (or multiparticle) coherence is extremely sensitive to external influence and has been observed only on the femto-second time-scale (and below) with specialized techniques. Some examples from work on Nb- and Y-hydrides will be discussed.

Keywords: Quantum coherence; Protons; Metal hydrides

1. Background

Studies of quantum coherence of protons in metal hydrides have a fairly long history, but they have up to now been limited to tunneling states of single protons trapped in double potential wells [1] or more complicated 4T or 6T configurations [2]. For a proton (or a positive muon, which has often been used a mock-up for the proton) in a double well of the type illustrated in Fig. 1, the wave-function is expressed as a superposition:

$$\Psi_{\pm} = (1/\sqrt{2})\{\phi(1) \pm \phi(2)\} \quad (1)$$

where $\phi(1)$ and $\phi(2)$ are functions localized at sites (1) and (2), respectively. This coherent state of the isolated quantum system is gradually reduced by wave-function collapse when the system is open to interaction with the environment and after a characteristic 'decoherence time' τ_{coh}, the particle is likely to be found in site (1) or site (2). For protons in metal hydrides the dominating decoherence mechanisms are interactions with phonons and conduction electrons, which lead to random fluctuations of the relative quantum phases of the functions $\phi(1)$ and $\phi(2)$ in Eq. (1). When temperature is lowered, these interations are expected to vary as T^3 and T, respectively, which means that the conduction electron mechanism remains even if the temperature is lowered to very low values. It was shown by inelastic neutron scattering [1] and by μ SR [3,4] around 1990 that coherence could still be restored in the metallic systems if the host metals were superconducting. This means that the connection to the electronic environment was cut off by the presence of the energy gap, which strongly reduced the number of active Fermi surface electrons and changed τ_{coh} from an estimated value $< 10^{-10}$ s to more than 10^{-6} s for tunneling systems with positive muons at $T = 0.1$ K.

The present report deals with the more complicated problem of quantum coherence in two- or multiparticle proton states. In principle, all interacting quantum systems (particles and fields) must be described by superposition states when viewed over sufficiently short times where decoherence has no time to act. However, estimates by Joos and Zeh [5] and Tegmark [6] indicate that even for a grain of dust on the μm-scale a total quantum superposition state of the system, which may exist momentarily, survives only for times of the order of 10^{-20} s or less. In the following we consider two (or a few) protons in a hydride as the "local system" and the

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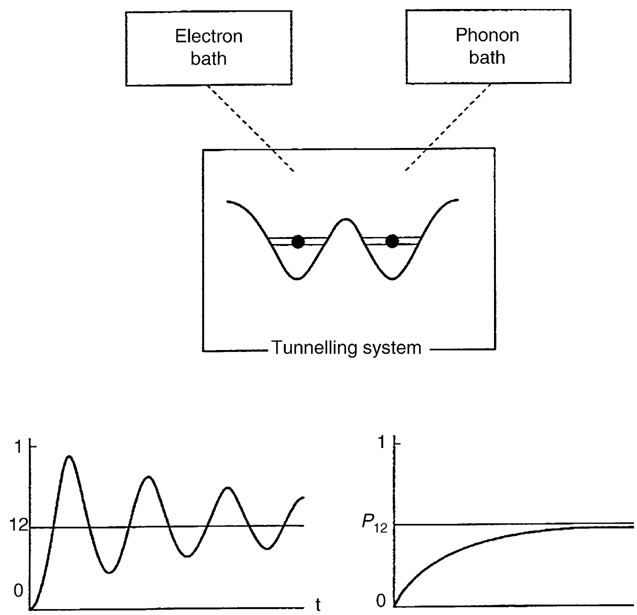

Fig. 1. A proton (or a positive muon) in a tunneling state, connected to a phonon bath and an electron bath. The lower part shows the probability $P_{12}(t)$ of finding the particle in well (2) after starting in well (1) with moderate damping (left) and for the case of overdamping (right).

rest (phonon and electronic degrees of freedom, as well as other protons) as the "environment". Such a small local system may stay coherent over about 10^{-15} s and be accessible to measurements which can display its coherence.

General multiparticle systems are entangled, which means that the total wave-function of particles α, β, ... occupying sites (1), (2), ... cannot be represented as simple products of the type $\Psi = \phi_1(\alpha)\phi_2(\beta)$ For a simple two-particle system it would instead have the form $\Psi(1,2) = A_{12}\phi_1(\alpha)\phi_2(\beta) + A_{21}\phi_1(\alpha)\phi_2(\beta)$ where A_{ik} are multiplying complex functions representing some entangling field (phononic, electronic or other) through which both particles are coupled. The simplest example of a non-separable wave-function is the one valid for a two-proton system:

$$\psi(\alpha,\beta)=(1/\sqrt{2})\{\phi_1(\alpha)\phi_2(\beta)+\zeta\phi_1(\beta)\phi_2(\alpha)\}\chi_M(\alpha,\beta) \quad (2)$$

which is non-separable because of the required anti-symmetrization for indistinguishable particles. Here the spinor $\chi_M^J(\alpha,\beta)$ to which their orbital function is coupled determines the sign of the coefficient $\zeta = (-1)^J$. Scattering on such a system, in which each of the particles gives contributions to the scattering matrix element when associated with both sites (1) and (2), involves a type of interference terms which are not present for separable particles.

In analogy with the smearing out of the phase factor in Eq. (1) by interaction with random fields, the coefficient ζ in Eq. (2) will also be multiplied with random phase factors and collapse to a simple product state after a decoherence time τ_{coh}. An estimate of τ_{coh} for the entanglement of a particular, well-defined system [7] will be mentioned later in this paper.

2. Neutron Compton scattering

Neutron scattering is normally performed with thermal neutrons (≈0.02 eV), which in most arrangements have an interaction time of the order of 10^{-13} to 10^{-12} s. The neutrons see therefore all nuclei as separable quantum units and no information can be obtained about superpositions (an exception is scattering on liquid H_2 molecules at low temperature, where the non-separability caused by the exchange interaction in Eq. (2) still survives and makes the cross-section for para-H_2 considerably smaller than that of two separable protons [8]).

In Compton scattering of neutrons, initial energies of the order of 10–100 eV are used and a considerable fraction of the available energy is imparted to the scattering nucleus (of mass M) which recoils and leaves the system as illustrated in Fig. 2a. If there is a sharp energy selection of the outgoing neutrons, there is (for each M in a compound system) a definite relation between the initial neutron velocity and the scattering angle θ. This means that the total neutron time-of-flight has a specific value for each M as shown in Fig. 2b. The intrinsic motion of the scattering nuclei broadens these lines which results in a characteristic Compton profile K(p), but the area A of each peak is proportional to the scattering cross-section so that A(M)/A(M′) are expected to be equal to the stoichiometric ratio M/M′ in the sample, multiplied with the tabulated ratio σ(M)/σ(M′).

Another feature of neutron Compton scattering is that the time for the scattering event, τ_{sc}, is proportional to M, but lim-

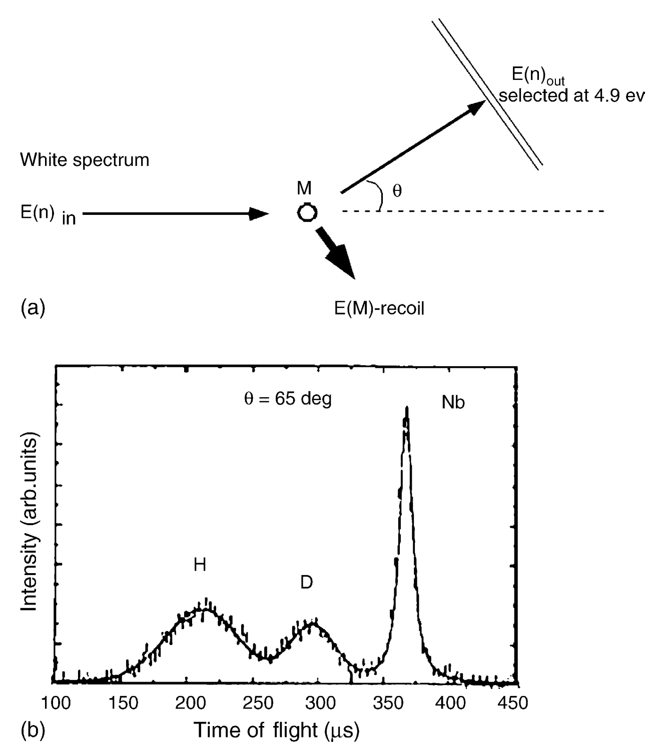

Fig. 2. (a) The principle of neutron Compton scattering and (b) time-of-flight spectrum for neutrons detected at a specific angle.

ited [9,10] by the values of the momentum transfer $q(\theta)$ and the momentum spread in the intrinsic motion $\sqrt{\langle p^2\rangle}$: $\tau_{sc} = \hbar M/[q(\theta)\sqrt{\langle p^2\rangle}]$. For typical values of $\sqrt{\langle p_{\rm H}^2\rangle}$ and $\sqrt{\langle p_{\rm D}^2\rangle}$ in metal hydrides, the scattering times fall in the 10^{-16} to 10^{-15} s range (Fig. 3), which means that observations of sub-fs phenomena are possible. It can also be calculated that the coherence length of these neutrons, energy selected by Au- or U-resonance foils, are still of the order of a few Ångströms, which means that each incoming neutron may interact with two (or a few) protons in our "local system" [11].

The first observations that H-systems behaved anomalously (i.e showing area ratios A(H)/A(M′) different from tabulated cross-section ratios σ(H)/σ(M′) were made by Chatzidimitriou-Dreismann et al. [12] on protons and deuterons in partly deuterated water. They showed A(H)/A(D) ratios 20–40% lower than expected. When the same method was first applied to protons and deuterons in a metal hydride (Karlsson et al. [13,14]) similar effects were seen in the A(H)/A(Me)-ratios. One of the purposes of studying Nb-hydrides was that hydrogenated Nb-foils could be made self-supporting which made the results free from correction for containers, another was that A(H)/A(Me) and A(D)/A(Me)-ratios could be obtained separately which provides information whether the anomalies should be referred to the scattering on H or D or both.

Some of the results are shown in Figs. 4 and 5, which are plotted as area ratios, normalized to one-to-one ratios of H/Nb and D/Nb. According to standard tables these area ratios are expected to be 13.1 and 1.26, respectively. The A(H)/A(Me)-ratios were found to be strongly reduced for all H and D concentrations, while the A(D)/A(Me)-ratio was reduced by less than 10% (Fig. 2b). A comparison with Fig. 3 shows that such a behaviour would indeed be expected if the anomaly were due to a short time phenomenon, valid only for times below 10^{-15} s, since all the deuteron data fall above this limit. An important observation is also that the A(H)/A(Me)-ratios are dependent on the scattering angle θ for the neutrons; the anomaly being considerably stronger for $\theta > 60°$, which corresponds to the shortest scattering times.

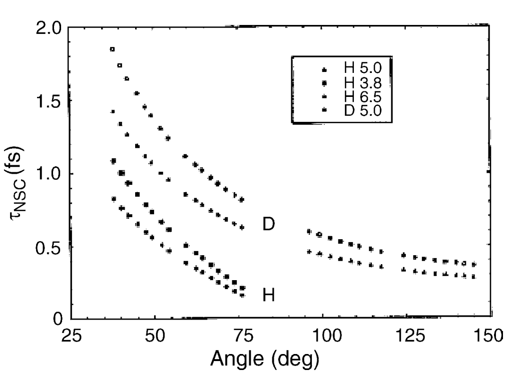

Fig. 3. Characteristic times for scattering on protons and deuterons at different angles. Two typical values are chosen for the intrinsic widths of the peaks.

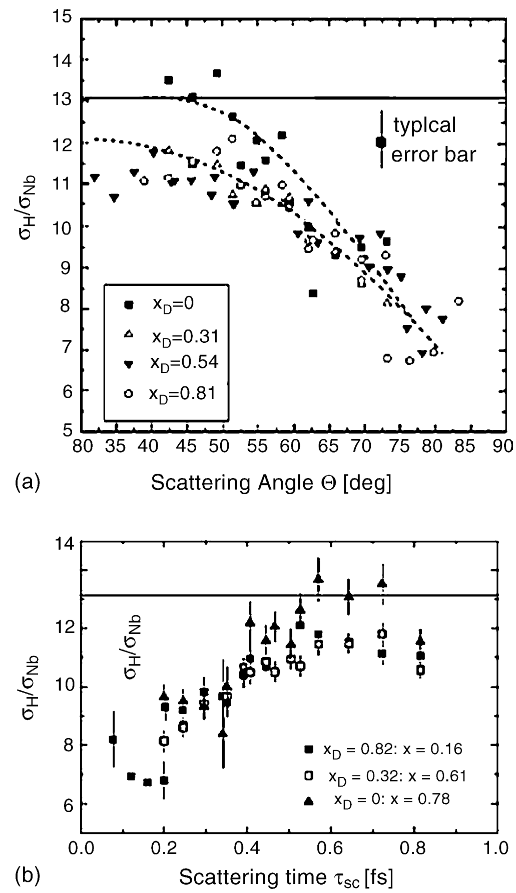

Fig. 4. (a) Angular dependence of $\sigma_{\rm H}/\sigma_{\rm Nb}$ for pure Nb–H and some mixed Nb–H–D hydrides (horizontal line represents the tabulated value) and (b) the same data converted to time-dependence. $X_{\rm D}$ is the D-content.

By use of the relation $\tau_{sc} = \hbar$M/[q(θ) $\sqrt{\langle p^2\rangle}$] mentioned above, the θ-dependence can be converted to a τ_{sc} (i.e. an observation time) dependence [13], which shows that the neutron cross-sections gradually approach the tabulated, individual particle values with time. This is a behaviour ex-

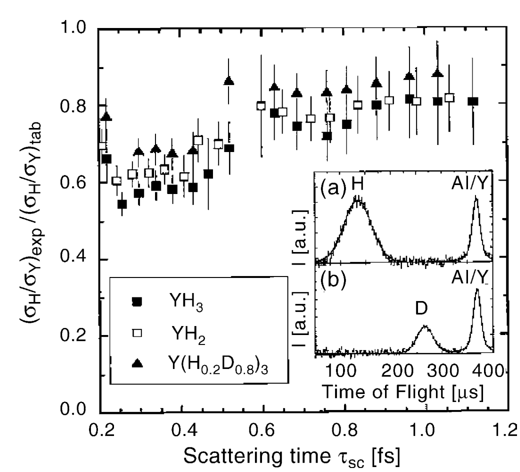

Fig. 5. Time-dependence for $\sigma_{\rm H}/\sigma_{\rm Y}$ for three different samples (normalized to tabulated values). The inset shows some typical time-of-flight spectra.

pected if the anomalies are connected with destructive interferences due to proton–proton entanglement; after a decoherence time of the order of 10^{-15} s, such interferences would disappear. Therefore, if the anomalies are indeed related to H–H entanglement, Compton scattering provides us with a method to study both their magnitude and their decoherence. A similar set of data has been collected [15] for Y-hydrides (Fig. 5). It remains to provide a quantitative treatment of entanglement-related cross-section reduction under Compton scattering conditions. A first attempt will be reviewed in the next section.

3. Interferences in neutron Compton scattering

A quantitative theoretical model has so far only been formulated for the simple case of scattering on two identical particles whose intital wave-function is non-separable and described by Eq. (2) above. The scattering matrix element $\langle f|V|i\rangle$ is obtained, straight-forwardly, by applying the scattering operator:

$$V = b_\alpha \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_\alpha) + b_\beta \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_\beta) \tag{3}$$

and assuming the following form of the wave-function for the final state:

$$\langle|f\rangle> = (1/\sqrt{2})\{\psi(\alpha)\exp(i\boldsymbol{p}'\cdot\boldsymbol{R}_\beta) + \zeta'\psi(\beta)\exp(i\boldsymbol{p}'\cdot\boldsymbol{R}_\alpha)\}\chi^{J'}_{M'}(\alpha,\beta) \tag{4}$$

Here, one of particles (α or β) is leaving the scattering site in the form of a plane wave with momentum $\boldsymbol{p}' = \boldsymbol{p}+\boldsymbol{q}$. The parameter $\zeta = (-1)^{J'} \neq \zeta$ if a spin-flip has occured. This state is still entangled and the particles α and β must be treated symmetrically, as long as decoherence has not occured. The function $\psi(\alpha) = T_1\phi(\alpha) + T_2\phi(\alpha)$, and similar expression for $\psi(\beta)$, describes the state of the remaining particle which still has amplitudes in both sites, now with relative amplitudes T_1/T_2 determined by ζ, since the total spin of the coupled system is J'.

The scattering matrix elements were shown in Refs. [11] to be reduced to:

$$< f|V|i > = (1/\sqrt{2})\{\chi^{J'}_{M'}(\alpha,\beta)[b_\alpha + \zeta\zeta' b_\beta]\chi^{J}_{M}(\alpha,\beta)\} \times K(\boldsymbol{p})[T_2 + \zeta\exp(-i\boldsymbol{p}\cdot\boldsymbol{d})T_1] \tag{5}$$

where $d = \boldsymbol{R}_1 - \boldsymbol{R}_2$. The square $[K(\boldsymbol{p})]^2$ is the well-known Compton profile, which describes the shape and width of the peaks in Fig. 2b. The integrals involving $\boldsymbol{q}\cdot\boldsymbol{d}$ disappear in the calculation, as expected for high momentum transfers but the term in $\boldsymbol{p}\cdot\boldsymbol{d}$ remains since $p << q$.

The cross-section will depend on the parameters ζ, ζ' (and therefore implicitly on the relative probability of coherent and incoherent cross-sections) and the direction of **p** relative to **d**, i.e. the vibrational state of the particles. It is is lower than the sum of two separable protons, which can be understood by considering the illustration in Fig. 6: The recoiling par-

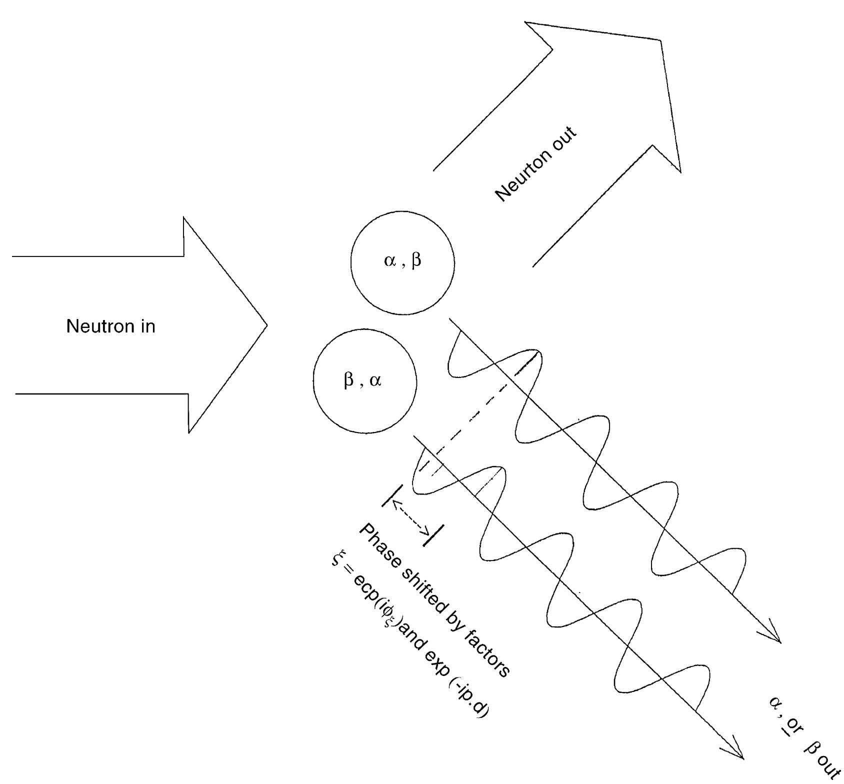

Fig. 6. Partial wave representation of a delocalized nucleus recoiling from two different sites. Absence of phase shift would correspond to full scattering intensity.

ticle wave (for α or β) has contributions starting from both sites, but these two partial waves are phase shifted by the factor exp(-iϕ_ζ), where ϕ_ζ is equal to 0 for $J = 0$ and π for $J = 1$, as well as by the factor $\exp(-i\boldsymbol{p}\cdot\boldsymbol{d})$. They interfere constructively to give the full single particle cross-section only when both factors are identical to one. We note here that this argument can be generalized to the case of scattering on a two-particle state with any form of non-separable orbital function $\{A_{12}\phi_1(\alpha)\phi_2(\beta) + A_{21}\phi_1(\beta)\phi_2(\alpha)\}$, where the ratio of the two complex amplitudes A_{21} and A_{12} would correspond to the factor ζ above.

Explicit expressions for the cross-section reductions for H–H pairs and D–D pairs can be found in Ref. [11] for certain parameter choices. Depending on the geometrical factor and the ratios of $\sigma_{\text{coh}}/\sigma_{\text{incoh}}$ the predictions fall in the range (0.4–0.6)σ_{H} for protons in H–H pairs and (0.7–0.9)σ_{D} for deutrons in D–D pairs. No calculations have been performed up to now for entangled three- or multiparticle configurations but the expectation is that the interference effects will be reduced, which would be in agreement with the 20–30% reductions observed at short times in the metal hydrides.

Most of the data show a clear tendency to approach standard cross-sections for quantum separable nuclei with increasing observation time τ_{sc}. This is expected as decoherence mechanisms are setting in around 10^{-15} s. No estimates have been performed up to now for the intrinsic decoherence rate of H–H entanglement in a metal hydride environment, but an an explicit calculation leading to $\tau_{\text{coh}} \approx 10^{-14}$ s has been performed for H–H pairs in liquid water which are perturbed by fluctuations in the H-bonding [7]. Fluctuations in the phonon or electron baths might give rise to similar values for the hydrides, but it should be remembered that decoherence in Compton scattering is also strongly mesurement-induced (by shake-up effects), which enter already on the 10^{-15} s scale. H–H dimer coherence has been found to exist for essentially longer times by the less perturbing thermal neutron scattering in the system $KHCO_3$ [16].

4. Conclusions

Metal hydrides have been found to be suitable environments for the study of a basic quantum phenomenon, namely the internal quantum phase relations between two or more particles. Such effects are expected to be observed even in condensed matter if they can be studied with time windows of femto-seconds or less.

Several recent experiments on Me–H, Me–D and mixed systems Me–H–D using the neutron Compton scattering method have shown strong anomalies in H-cross-sections which can be interpreted as effects of the specific interferences appearing when protons are entangled and cannot be represented by separable wave-functions. It has also been possible to follow the time-dependence of these effects in the sub-femto-second range, giving indications of the rate of coherence loss, i.e. the decoherence times. A simple theoretical model, valid for scattering on two identical particles (protons or deuterons) has been presented and gives a reasonable agreement with the experimental data. These studies may open up a so far unaccessible region of ultra-short times for further experimental and theoretical work.

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