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The role of the electronic degrees of freedom in neutron Compton scattering from molecular systems

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Abstract

We show that the standard treatment of deep inelastic neutron scattering from molecules implicitly assumes the adiabatic approximation for both initial and final states. Since the use of this approximation in the aforementioned scattering regime has recently been questioned, we propose a calculation scheme free from the adiabatic assumption in the final molecular state. This scheme generalizes the Gersch–Rodríguez–Smith approach, explicitly including the electronic degrees of freedom and the Coulomb interaction, and provides analytical formulae for the asymptotic response function and for the first final state effect correction. A practical calculation is performed on the simple H₂ molecule. Results show an asymptotic term very close to the standard one, but a first final state effect term (that is proportional to the inverse of the momentum transfer) exhibiting large discrepancies with respect to its equivalent derived from a semi-empirical internuclear potential.

1. Introduction

Deep inelastic neutron scattering is a spectroscopic technique able to probe atomic momentum distributions in condensed matter [1]. It is based on the so-called *impulsive approximation* (IA) [2], where the neutron–nucleus scattering time becomes so short (as the energy transfer grows) that the recoil of the hit nucleus can be reasonably assumed rid of interactions with neighbour particles. Considering the formal analogy with the well-known Compton scattering (i.e. x-ray photons inelastically deflected by core electrons [3]), it is quite common to use the term *neutron Compton scattering* (NCS) too. However, despite its simplicity, NCS is still affected by the unsolved problem of the anomalous deficit of proton cross-section in various compounds [4], which seems to resist several theoretical efforts [5] and experimental tests [6]. The anomalous cross-section deficit and its potentially disruptive effect on the standard neutron scattering theory [7] are not a real obstacle to the use of NCS as a routine technique in molecular applications. As a matter of fact, a reduction in the intensity of the proton recoil peak appears to be a quantitative

phenomenon directly affecting the absolute measurements only, and is drawn into the domain of standard spectroscopy merely by comparing recoil peaks from different elements or isotopes. Nevertheless the various attempts to provide a sound explanation of the aforementioned proton anomaly forced a few scientists to have a closer look at NCS from molecular systems, trying to overcome the usual 'spring-and-ball' approach [8] (dating back to 1967), which is a simple extension of the treatment employed in vibrational spectroscopy [9] and does not capture the full potential of an ultra-fast technique like NCS. In this way the situation has recently started to change: new studies have started to consider various unusual aspects of NCS, the most relevant of which is surely the role of the electronic dynamics beyond the limit of the Born–Oppenheimer approximation [10] and its possible link with the proton cross-section deficit.

The situation in NCS just described prompted the authors of the present study to explore the general role of the electronic degrees of freedom in deep inelastic neutron scattering from molecular systems, achieving new and more general expressions. Subsequently a toy-model (namely a single H₂

molecule) will be presented. Actually this molecule exhibits the simplest possible structure allowing straightforward and reliable simulations, but is already interesting in NCS as proved by the abundant literature on it (mentioned in [1]). Consequently, the rest of the work will be organized as follows: section 2 will contain the theory of the electronic degrees of freedom in neutron Compton scattering from molecules. Section 3 will present the calculations worked out implementing the equations of the previous section in the case of an isolated H₂ molecule, and finally section 4 will deal with the discussion of the obtained results and the conclusions.

2. Electronic degrees of freedom and neutron Compton scattering

In the vast literature on condensed matter, quantum mechanical calculations of thermal neutron scattering from nuclei (not involving magnetic structures and excitations) are practically always accomplished in the framework of the well-known adiabatic approximation of the total system wavefunction, Ψ [11]. If we consider a molecule composed of N nuclei and n electrons, represented by their position operators $\vec{R}_1, \dots, \vec{R}_N$ and $\vec{r}_1, \dots, \vec{r}_n$, respectively, then crudely assuming the adiabatic approximation (and paying no attention to the particle spins), one writes

$$\begin{aligned} \Psi_k(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \\ = \chi_v^{(e)}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \\ \times \phi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N), \end{aligned} \quad (1)$$

where ϕ_e depends on $\vec{R}_1, \dots, \vec{R}_N$ only parametrically, as represented by the semi-colon: $\phi_e(\dots; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)$. This implies that the two following independent orthonormalization rules apply:

$$\begin{aligned} \langle \phi_{e'}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \\ \times \phi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \rangle_{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n} = \delta_{e, e'}, \end{aligned} \quad (2)$$

and

$$\begin{aligned} \langle \chi_{v'}^{(e)}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) | \chi_v^{(e)}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \rangle_{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N} \\ = \delta_{v, v'}, \end{aligned} \quad (3)$$

where the external coordinates specify the integration variables and will often be dropped in what follows. If the tiny electron-neutron cross-section [12] is neglected ($\sigma_{n-e} \sim 10^{-35}$ m²), the possibility of electronic excitation through neutron scattering from the i th nucleus is controlled by the matrix elements $M_{k' \leftarrow k}^{(i)}(\vec{Q})$ (with \vec{Q} being the wavevector transfer) of this sort

$$M_{k' \leftarrow k}^{(i)}(\vec{Q}) = \langle \Psi_{k'} | \exp(i\vec{Q} \cdot \vec{R}_i) | \Psi_k \rangle, \quad (4)$$

which, in the adiabatic approximation, reads

$$\begin{aligned} M_{e', v' \leftarrow e, v}^{(i)}(\vec{Q}) = \langle \chi_{v'}^{(e')} \phi_{e'} | \exp(i\vec{Q} \cdot \vec{R}_i) | \chi_v^{(e)} \phi_e \rangle \\ = \delta_{e, e'} \langle \chi_{v'}^{(e)} | \exp(i\vec{Q} \cdot \vec{R}_i) | \chi_v^{(e)} \rangle, \end{aligned} \quad (5)$$

meaning that no electronic excitation from e to $e' \neq e$ is possible via neutron scattering from nuclei. So the possibility to excite electronic states through neutron scattering has to

be related to a hypothetical non-adiabatic nature of the initial and/or final states of the molecule hit by neutrons.

Naturally in case of low temperature (T) and modest values of the energy transferred from the neutron to the system ($\hbar\omega$), the number of initial (k) and final (k') states relevant in the scattering process is small. In such a situation it is, at least conceptually, possible to verify the well-known criterion for the adiabatic approximation to hold for each pair of initial and final states. Namely the adiabatic approximation can be trusted whenever the various potential energy surfaces, $W_e(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)$ (obtained as eigenvalues from the solution of the electronic Schrödinger equation for the eigenstates ϕ_e) are well separated:

$$W_{e=0}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \ll W_{e=1}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \ll \dots \quad (6)$$

for all the $\vec{R}_1, \dots, \vec{R}_N$ values explored by the nuclei in the molecule. However, when $\hbar\omega$ and Q increase (for example as in NCS), the number of final states involved in the scattering process grows very rapidly. One has to consider all the k' states whose energies $E_{k'}$ roughly satisfy the inequation:

$$\begin{aligned} E_k + \frac{\hbar^2 Q^2}{2M_i} - 2 \left(\frac{2\hbar^2 Q^2}{3M_i} \langle T_i \rangle \right)^{1/2} < E_{k'} \\ < E_k + \frac{\hbar^2 Q^2}{2M_i} + 2 \left(\frac{2\hbar^2 Q^2}{3M_i} \langle T_i \rangle \right)^{1/2}, \end{aligned} \quad (7)$$

with $\langle T_i \rangle$ and M_i being the i th-nucleus mean kinetic energy and mass, respectively. Thus the most common situation in a typical NCS experiment from molecules is the following: given the relatively low temperature of the measurement the relevant initial states Ψ_k are often only one, which coincides with the system ground state Ψ_0 and is generally fairly well described by the adiabatic approximation $\Psi_0 = \chi_{v=0}^{(e=0)} \phi_{e=0}$. On the contrary, the relevant final states $\Psi_{k'}$ are numerous and practically unknown, so that the validity of the adiabatic approximation for them becomes highly disputable, especially when the scattering time [13] $\tau_s = \pi \left(\frac{2Q^2}{3M_i} \langle T_i \rangle \right)^{-1/2}$, shrinks so much to come close to the typical electronic ‘rearrangement’ time (i.e. 10^{-18} s). This is a crucial point since the large majority of the NCS work on molecular systems done so far is just based on the adiabaticity of $\Psi_{k'}$ in an implicit way.

In order to cope with this problem let us focus on the scattering (self) from a proton belonging to the target-molecule (kept at $T = 0$) and labelled by ‘1’. It is worthwhile to introduce the West-transformed intermediate scattering function, $\tilde{F}(s, \vec{Q})$:

$$\tilde{F}(s, \vec{Q}) = \exp\left(-i\frac{sQ}{2}\right) I_s(\vec{Q}, t), \quad (8)$$

where s is the proton mean travelled path, $s = \frac{\hbar Q}{M_1} t$, and $I_s(\vec{Q}, t)$ is the usual intermediate scattering function (self) as defined in the literature [14], depending on time t . It is worth noting that in the present high- Q regime all the distinct terms in the scattering law can be safely neglected (i.e. the incoherent approximation [15] holds), so that the total intermediate scattering function and its self-counterpart actually coincide. Following a well-known standard procedure [16], it is possible

to cast $I_s(\vec{Q}, t)$ in such a way to get rid of the final molecular states:

$$I_s(\vec{Q}, t) = \langle \Psi_0 | \exp[i\hbar^{-1}H(\vec{P}_1 + \hbar\vec{Q}, \vec{P}_2 \dots)t] \times \exp[-i\hbar^{-1}H(\vec{P}_1, \vec{P}_2 \dots)t] | \Psi_0 \rangle, \quad (9)$$

where H is full molecular Hamiltonian (decomposed in nuclear kinetic T_N , electronic kinetic T_e , and potential V terms):

$$H(\vec{P}_1, \dots, \vec{p}_1, \dots, \vec{R}_1, \dots, \vec{r}_1, \dots) = T_N(\vec{P}_1, \dots, \vec{P}_N) + T_e(\vec{p}_1, \dots, \vec{p}_n) + V(\vec{R}_1, \dots, \vec{R}_N, \vec{r}_1, \dots, \vec{r}_n). \quad (10)$$

In the two equations above the usual notation has been employed: \vec{P}_i is the momentum of the i th nucleus, while \vec{p}_j that of the j th electron, having mass m_e and charge e . In addition, Z_i and ϵ_0 stand for the atomic number of the i th nucleus and the vacuum dielectric constant, respectively. From equation (10) one easily derives

$$H(\vec{P}_1 + \hbar\vec{Q}, \vec{P}_2 \dots) = H(\vec{P}_1, \vec{P}_2 \dots) + \frac{\hbar^2\vec{Q} \cdot \vec{P}_1}{M_1} + \frac{\hbar^2Q^2}{2M_1}, \quad (11)$$

from which, since \vec{Q} is only a c -number (vector), the following expression for $\tilde{F}(s, \vec{Q})$ can be worked out:

$$\tilde{F}(s, \vec{Q}) = \langle \Psi_0 | \exp\left[i\frac{M_1s}{\hbar^2Q}H(\vec{P}_1, \vec{P}_2 \dots) + is\hat{Q} \cdot \vec{P}_1\right] \times \exp\left[-i\frac{M_1s}{\hbar^2Q}H(\vec{P}_1, \vec{P}_2 \dots)\right] | \Psi_0 \rangle, \quad (12)$$

where $\hat{Q} = \vec{Q}/Q$. Following [17] and developing $\tilde{F}(s, \vec{Q})$ in a power series of Q^{-1} :

$$\tilde{F}(s, \vec{Q}) = \sum_{k=0}^{\infty} \left(\frac{M_1}{\hbar^2Q}\right)^k \tilde{F}_k(s, \hat{Q}), \quad (13)$$

one arrives to a simple expression for the asymptotic term, $\tilde{F}_0(s, \hat{Q})$, i.e. the only surviving term in the Q^{-1} series as Q grows to infinite:

$$\tilde{F}_0(s, \hat{Q}) = \langle \Psi_0 | e^{is\hat{Q} \cdot \vec{P}_1} | \Psi_0 \rangle = \langle \Psi_0(\vec{R}_1, \vec{R}_2 \dots, \vec{r}_1, \dots) | \times \Psi_0(\vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots, \vec{r}_1, \dots) \rangle. \quad (14)$$

So far our treatment has been exact, since the Coulomb potential is Fourier transformable and so the expansion of equation (13) (named GRS expansion) is fully justified [17]. However, if the adiabatic approximation is now assumed for Ψ_0 only (where it can be verified), one finally writes the asymptotic term in a more amenable and computable way:

$$\tilde{F}_0(s, \hat{Q}) = \int d\vec{R}_1 \dots \int d\vec{R}_N \chi_0^{(0)*}(\vec{R}_1, \vec{R}_2 \dots) \times \chi_0^{(0)}(\vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots) \int d\vec{r}_1 \dots \int d\vec{r}_n \phi_0^*(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots) \phi_0(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots). \quad (15)$$

Similarly to equation (14), but using a longer algebraic treatment [17], one can derive an expression for $\tilde{F}_1(s, \hat{Q})$:

$$\tilde{F}_1(s, \hat{Q}) = i\langle \Psi_0 | \int_0^s d\zeta [V(\vec{R}_1 + \zeta\hat{Q}, \vec{R}_2 \dots, \vec{r}_1, \vec{r}_2 \dots) - V(\vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots, \vec{r}_1, \vec{r}_2 \dots)] e^{is\hat{Q} \cdot \vec{P}_1} | \Psi_0 \rangle, \quad (16)$$

where the full Coulombian potential energy, V , can be safely replaced by V_1 , its component explicitly depending on the 1st-nucleus position (see equation (10)):

$$V_1(\vec{R}_1, \vec{R}_2 \dots, \vec{r}_1, \vec{r}_2 \dots) = \sum_{i>1} \frac{Z_1 Z_i e^2}{4\pi\epsilon_0 |\vec{R}_1 - \vec{R}_i|} - \sum_j \frac{Z_1 e^2}{4\pi\epsilon_0 |\vec{R}_1 - \vec{r}_j|}. \quad (17)$$

This replacement is exact since the Coulomb potential is pairwise additive and all the coordinate operators are evaluated at the same time ($t = 0$) and so they commute. It is now worth comparing equations (14) and (16) to the respective standard expressions used in the NCS theory [18] and obtained forbidding any electronic excitation in the scattering process, i.e. assuming the adiabatic approximation for all the final molecular states (as in equation (5)):

$$\tilde{F}_0^{(st)}(s, \hat{Q}) = \langle \chi_0^{(0)} | e^{is\hat{Q} \cdot \vec{P}_1} | \chi_0^{(0)} \rangle = \int d\vec{R}_1 \dots \int d\vec{R}_N \chi_0^{(0)*}(\vec{R}_1, \vec{R}_2 \dots) \times \chi_0^{(0)}(\vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots); \quad (18)$$

$$\tilde{F}_1^{(st)}(s, \hat{Q}) = i\langle \chi_0^{(0)} | \int_0^s d\zeta [V_N(\vec{R}_1 + \zeta\hat{Q}, \vec{R}_2 \dots) - V_N(\vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots)] e^{is\hat{Q} \cdot \vec{P}_1} | \chi_0^{(0)} \rangle, \quad (19)$$

where $V_N(\vec{R}_1, \vec{R}_2 \dots)$ coincides with the potential energy surfaces of the electronic ground state ϕ_0 , namely $W_{e=0}(\vec{R}_1, \vec{R}_2 \dots)$, plus the so-called *adiabatic correction*, $H'_{0,0}(\vec{R}_1, \vec{R}_2 \dots)$ [19]:

$$H'_{0,0}(\vec{R}_1, \vec{R}_2 \dots) = \int d\vec{r}_1 \dots \times \int d\vec{r}_n \phi_0^*(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots) T_N(\vec{P}_1, \dots, \vec{P}_N) \times \phi_0(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots). \quad (20)$$

It is not pointless to remind that in the framework of the Born–Oppenheimer approximation (slightly cruder than the adiabatic one), $H'_{0,0}$ is neglected all together in solving the nuclear Schrödinger equation for $\chi_v^{(e)}$ and, as a consequence, in the potential term V_N too.

It is now straightforward to prove that equation (15) coincides with its standard counterpart, namely with equation (18), if $\phi_0(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots)$ is replaced by $\phi_0(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots)$. As for the first GRS correction, in order to try reducing equation (16) to equation (19), one obviously has to make use of the same approximation as above. However this is not enough: an additional and coarse assumption has to be made too. According to the well-known molecular virial theorem [21], one can perform the electronic average on the full potential energy of the molecule obtaining

$$\langle \phi_0 | V | \phi_0 \rangle = 2W_{e=0} + \sum_i \vec{R}_i \cdot \vec{\nabla}_{\vec{R}_i} W_{e=0}, \quad (21)$$

which has to be compared to $V_N = W_{e=0} + H'_{0,0}$, employed in equation (19). The equivalence between the two functions, even neglecting the small adiabatic correction, is evidently

false, since $W_{e=0}(\vec{R}_1, \vec{R}_2 \dots)$ is not in general a homogeneous function of degree -1 (e.g. the Morse potential).

Giving up to the constraints that in NCS the final molecular states have to satisfy the adiabatic approximation, some empirically observable differences have already been produced in the formulae for the asymptotic scattering law and, even more, for the first GRS correction to it. However, in order to gain a deeper physical understanding of our result for $\tilde{F}_0(s, \hat{Q})$, it is useful to translate this into the momentum-space language. The relationship between the West-transformed intermediate scattering function and the 1st-nucleus momentum distribution [20], $N_1(\vec{P}_1)$, is simply given by

$$N_1(\vec{P}_1) = \frac{1}{8\pi^3} \int d\vec{X} \exp(-i\vec{X} \cdot \vec{P}_1) \tilde{F}_0(X, \hat{X}), \quad (22)$$

so that the 1st-nucleus mean kinetic energy $\langle T_1 \rangle$ reads

$$\langle T_1 \rangle = \int \frac{\hbar^2 P_1^2}{2M_1} N_1(\vec{P}_1) d\vec{P}_1 = -\frac{\hbar^2}{2M_1} [\nabla_{\vec{X}}^2 \tilde{F}_0(X, \hat{X})]_{\vec{X}=0}. \quad (23)$$

Thus equations (15) and (18) give rise to two different estimates of the single-nucleus momentum distribution, namely

$$\begin{aligned} N_1(\vec{P}_1) &= \frac{1}{8\pi^3} \int d\vec{X} \exp(-i\vec{X} \cdot \vec{P}_1) \\ &\times \int d\vec{R}_1 \dots \int d\vec{R}_N \chi_0^{(0)*}(\vec{R}_1, \vec{R}_2 \dots) \\ &\times \chi_0^{(0)}(\vec{R}_1 + \vec{X}, \vec{R}_2 \dots) \int d\vec{r}_1 \dots \\ &\times \int d\vec{r}_n \phi_0^*(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots) \\ &\times \phi_0(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1 + \vec{X}, \vec{R}_2 \dots), \end{aligned} \quad (24)$$

and

$$\begin{aligned} N_1^{(st)}(\vec{P}_1) &= \frac{1}{8\pi^3} \int d\vec{X} \exp(-i\vec{X} \cdot \vec{P}_1) \int d\vec{R}_1 \dots \\ &\times \int d\vec{R}_N \chi_0^{(0)*}(\vec{R}_1, \vec{R}_2 \dots) \chi_0^{(0)}(\vec{R}_1 + \vec{X}, \vec{R}_2 \dots), \end{aligned} \quad (25)$$

respectively. From these two equations, after some algebraic manipulation, one can extract the 1st-nucleus mean kinetic energy in the framework of two approximations:

$$\begin{aligned} \langle T_1 \rangle &= -\frac{\hbar^2}{2M_1} \int d\vec{R}_1 \dots \int d\vec{R}_N \chi_0^{(0)*}(\vec{R}_1, \vec{R}_2 \dots) \\ &\times \left[\nabla_{\vec{R}_1}^2 \chi_0^{(0)}(\vec{R}_1, \vec{R}_2 \dots) + \chi_0^{(0)}(\vec{R}_1, \vec{R}_2 \dots) \int d\vec{r}_1 \dots \right. \\ &\times \left. \int d\vec{r}_n \phi_0^*(\vec{r}_1, \dots; \vec{R}_1, \dots) \nabla_{\vec{R}_1}^2 \phi_0(\vec{r}_1, \dots; \vec{R}_1, \dots) \right]; \end{aligned} \quad (26)$$

$$\begin{aligned} \langle T_1 \rangle^{(st)} &= -\frac{\hbar^2}{2M_1} \int d\vec{R}_1 \dots \\ &\times \int d\vec{R}_N \chi_0^{(0)*}(\vec{R}_1, \vec{R}_2 \dots) \nabla_{\vec{R}_1}^2 \chi_0^{(0)}(\vec{R}_1, \vec{R}_2 \dots). \end{aligned} \quad (27)$$

It is immediate to verify that the difference between $\langle T_1 \rangle$ and $\langle T_1 \rangle^{(st)}$ is just the adiabatic correction for the 1st-nucleus

averaged over the nuclear coordinates:

$$\begin{aligned} \langle T_1 \rangle - \langle T_1 \rangle^{(st)} &= \frac{-\hbar^2}{2M_1} \int d\vec{R}_1 \dots \int d\vec{R}_N \int d\vec{r}_1 \dots \\ &\times \int d\vec{r}_n |\chi_0^{(0)}(\vec{R}_1, \vec{R}_2 \dots)|^2 \phi_0^*(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots) \\ &\times \nabla_{\vec{R}_1}^2 \phi_0(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots). \end{aligned} \quad (28)$$

Thus we have found that the standard NCS theory is not only potentially imprecise in describing the single-nucleus momentum distribution, given the absence of the electronic terms, but even the $N_1(\vec{P}_1)$ -second moment (proportional to the single-nucleus mean kinetic energy) might be slightly underestimated because of the lack of any averaged adiabatic correction.

In addition to this, another important result can be actually extracted from our calculation, namely the first two GRS-terms of the non-adiabatic correction to the NCS response function $F(y, \vec{Q})$, taken to be the one-dimensional Fourier transform of $\tilde{F}(s, \vec{Q})$:

$$F(y, \vec{Q}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds \exp(-iys) \tilde{F}(s, \vec{Q}). \quad (29)$$

After defining the non-adiabatic correction to the NCS response function as $F(y, \vec{Q}) - F^{(st)}(y, \vec{Q})$, one can expand it following equation (13) and write

$$\begin{aligned} F(y, \vec{Q}) - F^{(st)}(y, \vec{Q}) &= \sum_{k=0}^{\infty} \left(\frac{M_1}{\hbar^2 Q} \right)^k [F_k(y, \hat{Q}) - F_k^{(st)}(y, \hat{Q})], \end{aligned} \quad (30)$$

where, as reported earlier, the only approximation involved is the assumed adiabaticity of the molecular ground state. Of the equation above, we actually know the first two terms (namely $k=0$ and 1), given by the Fourier transforms of the differences between equations (15) and (18), and equations (16) and (19), respectively. Finally, after a rather longer mathematical effort [17, 22], it would be also possible to write the $k=2$ term.

Our treatment can become even more accurate if the possible non-adiabaticity of the initial molecular state is taken into account. In this case Ψ_0 can be decomposed in a linear combination of purely adiabatic states making use of $\{\vec{R}\}$ -dependent coefficients:

$$\begin{aligned} \Psi_0(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) &= \sum_e \alpha^{(e)}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \\ &\times \phi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N), \end{aligned} \quad (31)$$

where the limiting case of an adiabatic Ψ_0 is recovered through $\alpha^{(e)} = \chi_0^{(0)} \delta_{e,0}$. Plugging equation (31) into equations (15) and (16), one obtains

$$\begin{aligned} \tilde{F}_0(s, \hat{Q}) &= \sum_{e, e'} \int d\vec{R}_1 \dots \int d\vec{R}_N \alpha^{(e')*}(\vec{R}_1, \vec{R}_2 \dots) \\ &\times \alpha^{(e)}(\vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots) \int d\vec{r}_1 \dots \\ &\times \int d\vec{r}_n \phi_e^*(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1, \vec{R}_2 \dots) \\ &\times \phi_{e'}(\vec{r}_1, \vec{r}_2 \dots; \vec{R}_1 + s\hat{Q}, \vec{R}_2 \dots), \end{aligned} \quad (32)$$

and an analogous expression for $\tilde{F}_1(s, \hat{Q})$. Obviously this approach makes sense only if the number of e, e' -states included in the sum of equation (32) is small enough.

3. A very simple model of molecular systems: H₂

The simplest existing molecule, namely H₂, can be used as a practical example to evaluate the impact of the section 2 findings. Molecular hydrogen has been widely investigated through NCS, both theoretically and experimentally, so the standard deep inelastic neutron scattering description of this system is well-assessed, both in the framework of the IA [23–25], and making use of the exact final roto-vibrational states for the two nuclei [26, 27]. This will be very helpful when comparing results obtained in the framework of equations (15) and (18).

In what follows we will focus on a single para-hydrogen molecule, whose orbital wavefunction Ψ is a function of two nuclear coordinates \vec{r}_1 and \vec{r}_2 , and of two electronic coordinates $\vec{r}_{e,1}$ and $\vec{r}_{e,2}$, all measured in the *laboratory frame of reference* (LFoR). This wavefunction can be conveniently factorized in a *centre-of-mass* (CoM) term Θ times an intra-molecular term Φ :

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_{e,1}, \vec{r}_{e,2}) = \Theta(\vec{R}_{cm}) \Phi(\vec{R}, \vec{x}_{e,1}, \vec{x}_{e,2}), \quad (33)$$

where \vec{R}_{cm} is the centre-of-mass coordinate (obviously measured in the LFoR), while $\vec{R} = \vec{r}_1 - \vec{r}_2$ is the internuclear distance, which is of course invariant moving from the LFoR to the *centre-of-mass frame of reference* (CoM FoR). As for the new electronic coordinates $\vec{x}_{e,1}$ and $\vec{x}_{e,2}$, they are defined with respect to the nuclear middle point (very close but not coinciding with the CoM) as

$$\vec{x}_{e,1(2)} = \vec{r}_{e,1(2)} - \frac{1}{2}(\vec{r}_1 + \vec{r}_2), \quad (34)$$

and are still surely invariant moving from the LFoR to the CoM FoR. However, if the electronic coordinates in the CoM FoR are represented by $\vec{r}'_{e,1(2)}$ and λ is the ratio between the electron and the proton mass, then the following relationships hold in CoM FoR only:

$$\begin{aligned} \vec{x}_{e,1} &= \left(1 - \frac{\lambda}{2}\right) \vec{r}'_{e,1} - \frac{\lambda}{2} \vec{r}'_{e,2}, \\ \vec{x}_{e,2} &= \left(1 - \frac{\lambda}{2}\right) \vec{r}'_{e,2} - \frac{\lambda}{2} \vec{r}'_{e,1}. \end{aligned} \quad (35)$$

Being interested in a single H₂ molecule, let us focus on Φ or, more precisely, on the intra-molecular ground state, Φ_0 . Here we immediately face the problem of the validity of the Born–Oppenheimer approximation for Φ_0 , which has been dealt with in detail in [28]. However, let us leave it aside for the moment (it will be discussed in section 4) and assume the adiabatic approximation to hold:

$$\Phi_0(\vec{R}, \vec{x}_{e,1}, \vec{x}_{e,2}) = \phi_0(\vec{x}_{e,1}, \vec{x}_{e,2}; \vec{R}) \chi_0^{(0)}(\vec{R}), \quad (36)$$

where the same notation as in equation (15) has been employed. At this stage the two ground-state wavefunctions,

namely electronic and nuclear, are known in the literature. The former, spectroscopically labelled with the symbol $X^1\Sigma_g^+$, has been carefully evaluated for example in [29], where it is expressed as the sum of 249 terms for $|\vec{R}|$ ranging from 0.1 to 12.0 bohr (i.e. 0.053–6.350 Å). Once ϕ_0 is known together with its energy eigenvalue (both parametrically dependent on \vec{R}), the $\chi_0^{(0)}$ state can be directly obtained by solving the nuclear Schrödinger equation, which should also include, if the Born–Oppenheimer level of accuracy is not acceptable, the aforementioned adiabatic correction. The only delicate point is just the long form taken by this correction once it is written in the CoM FoR [19]; however, at least for two-electron diatomic homonuclear molecules, this can be done without approximations. The H₂ nuclear ground state, which is isotropic, is generally expressed as

$$\chi_0^{(0)}(\vec{R}) = (4\pi)^{-1/2} \frac{1}{R} u_{0,0}(R), \quad (37)$$

where $u_{0,0}(R)$ is the solution of a one-dimensional (reduced) Schrödinger equation and is labelled with $\nu = 0$ and $j = 0$, the vibrational and rotational quantum numbers, respectively. If a high level of accuracy is not needed, as in the present study, a simple form for $u_{0,0}(R)$ can be obtained from the Morse potential ground state [30]:

$$u_{0,0}(R) = N_{0,0} \exp(-\xi/2) \xi^s, \quad (38)$$

where

$$\xi = \left(\frac{2\sqrt{2\mu D}}{\alpha\hbar}\right) \exp[-\alpha(R - R_0)], \quad (39)$$

and where

$$s = \left(\frac{\sqrt{2\mu D}}{\alpha\hbar}\right) - \frac{1}{2}. \quad (40)$$

The above symbols have a simple physical meaning: $N_{0,0}$ is a normalization constant, μ is the two-proton reduced mass, R_0 is the equilibrium internuclear distance, while D and α , two parameters characterizing (together with R_0) the Morse potential $V_{N,M}(R)$, represent the potential well depth and curvature, respectively:

$$V_{N,M}(R) = D\{\exp[-2\alpha(R - R_0)] - 2\exp[-\alpha(R - R_0)]\}. \quad (41)$$

Making use of reduced intra-molecular wavefunction $u_{0,0}(R)$, and assuming a simple Maxwell–Boltzmann distribution for the molecular CoM velocities, it is possible to write down explicitly the West-transformed intermediate scattering functions of equations (18) and (19) in the framework of the standard approach:

$$\begin{aligned} \tilde{F}_0^{(st)}(s) &= \tilde{F}_0^{(st,cm)}(s) \int_0^\infty dR \int_{-1}^1 \frac{d\eta}{2} u_{0,0}(R) u_{0,0} \\ &\times \left(\sqrt{s^2 + R^2 - 2sR\eta}\right); \end{aligned} \quad (42)$$

$$\begin{aligned} \tilde{F}_1^{(st)}(s) &= i\tilde{F}_0^{(st,cm)}(s) \int_0^\infty dR \int_{-1}^1 \frac{d\eta}{2} u_{0,0}(R) u_{0,0} \\ &\times \left(\sqrt{s^2 + R^2 - 2sR\eta}\right) \\ &\times \int_0^s \left[V_{N,M} \left(\sqrt{s^2 + R^2 - 2\zeta R\eta}\right) \right. \\ &\left. - V_{N,M} \left(\sqrt{s^2 + R^2 - 2sR\eta}\right) \right] d\zeta, \end{aligned} \quad (43)$$

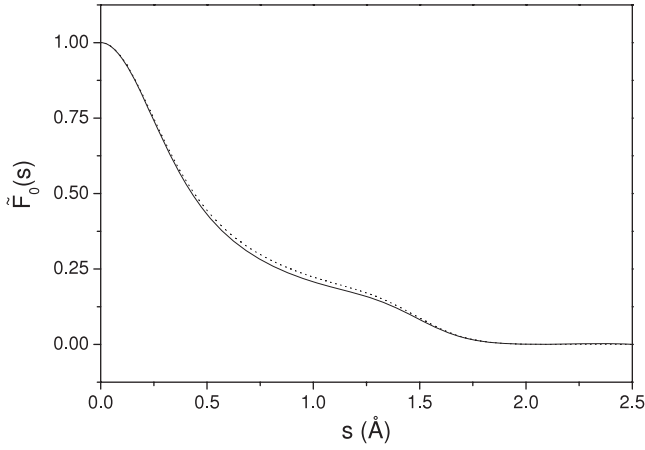


Figure 1. Asymptotic term of the West-transformed intermediate scattering function for gaseous para-hydrogen in the framework of the standard approach (dotted line), and including the electronic degrees of freedom (full line). The two calculations are performed at low temperature (i.e. in the molecular roto-vibrational ground state) and do not include any centre-of-mass thermal broadening.

where the intermolecular interactions have been neglected (due to the extremely diluted H₂ gas used in the present model), so that the CoM term is simply given by

$$\tilde{F}_0^{(\text{st,cm})}(s) = \exp\left(-\frac{s^2 M_{\text{H}}^2 \langle \vec{V}^2 \rangle}{2 3 \hbar^2}\right), \quad (44)$$

with M_{H} being the proton mass and $\langle \vec{V}^2 \rangle$ the mean square CoM velocity. Needless to say that the \hat{Q} dependence has been dropped because of the isotropic character of this model. Numerical results from equations (42) and (43) are reported, respectively, in figures 1 and 2 in the case of $\langle \vec{V}^2 \rangle = 0$, while their Fourier transforms, $F_0^{(\text{st})}(y)$ and $F_1^{(\text{st})}(y)$, respectively, in figures 3 and 4.

The inclusion of the electronic degrees of freedom in the asymptotic term of the West-transformed intermediate scattering function, as in equation (15), can be achieved in H₂ via the $f(s\hat{Q}, \vec{R})$ function:

$$f(s\hat{Q}, \vec{R}) = \int d\vec{x}_{e,1} \times \int d\vec{x}_{e,2} \phi_0^*(\vec{x}_{e,1}, \vec{x}_{e,2}; \vec{R}) \phi_0(\vec{x}_{e,1}, \vec{x}_{e,2}; \vec{R} + s\hat{Q}), \quad (45)$$

which in a diatomic molecule is actually a function of R , s , and η only: $f(s, R, \eta)$. Plugging equation (45) into equation (42), one obtains the H₂ asymptotic term of the West-transformed intermediate scattering function in the framework of the present approach including the electronic degrees of freedom:

$$\tilde{F}_0(s) = \tilde{F}_0^{(\text{st,cm})}(s) \int_0^\infty dR \times \int_{-1}^1 \frac{d\eta}{2} f(s, R, \eta) u_{0,0}(R) u_{0,0}(\sqrt{s^2 + R^2 - 2sR\eta}), \quad (46)$$

where once again the intermolecular interactions have been neglected. A similar treatment can be applied to the first GRS

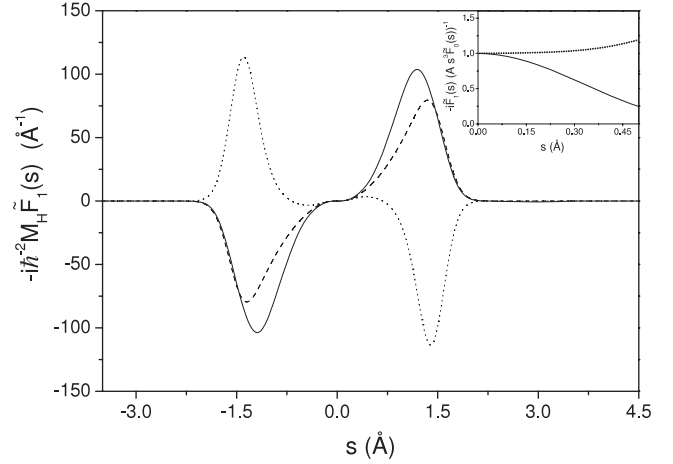


Figure 2. First final state effect term of the West-transformed intermediate scattering function for gaseous para-hydrogen in the framework of the standard approach (dotted line), and including the electronic degrees of freedom (full line). A third calculation, based on the Sears and Glyde model for final state effects (see the main text), is also plotted as a dashed line. The three calculations are performed at low temperature (i.e. in the molecular roto-vibrational ground state) and do not include any centre-of-mass thermal broadening. In the inset the ratios between the first two functions of the main figure and their respective low- s limits are reported (using the same graphical notation as the main picture).

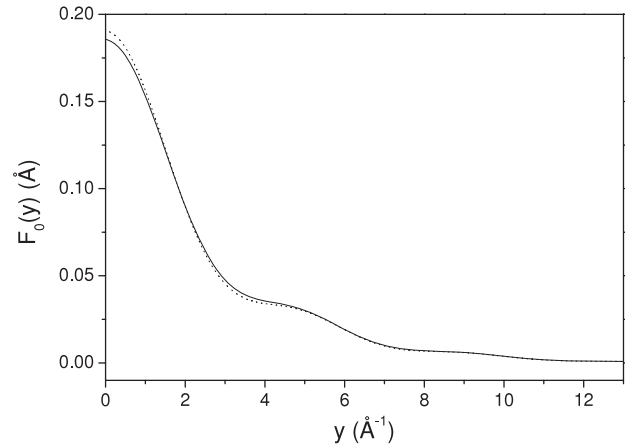


Figure 3. Asymptotic term of the West-scaled response function for gaseous para-hydrogen in the framework of the standard approach (dotted line), and including the electronic degrees of freedom (full line). The two calculations are performed at low temperature (i.e. in the molecular roto-vibrational ground state) and do not include any centre-of-mass thermal broadening.

term of the final state effect correction:

$$\tilde{F}_1(s) = i\tilde{F}_0^{(\text{st,cm})}(s) \int_0^\infty dR \times \int_{-1}^1 \frac{d\eta}{2} u_{0,0}(R) u_{0,0}(\sqrt{s^2 + R^2 - 2sR\eta}) \times \int_0^s [U(\zeta, R, s, \eta) - U(s, R, s, \eta)] d\zeta, \quad (47)$$

where the new intra-molecular potential function U , following equation (17), is composed of two parts: one purely nuclear,

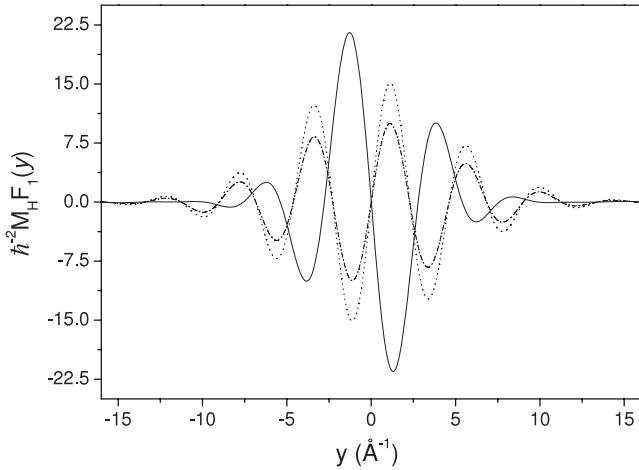


Figure 4. First final state effect term of the West-scaled response function for gaseous para-hydrogen in the framework of the standard approach (dotted line), and including the electronic degrees of freedom (full line). A third calculation, operated similarly to the first but using LCAO-approximated H₂ parameters, is also plotted as a dash-dotted line. The three calculations are performed at low temperature (i.e. in the molecular roto-vibrational ground state) and do not include any centre-of-mass thermal broadening.

and the other describing the electron–nucleus Coulomb interaction:

$$U(\zeta \hat{Q}, \vec{R}, s \hat{Q}) = f(s \hat{Q}, \vec{R}) \frac{e^2}{4\pi\epsilon_0 |\vec{R} + \zeta \hat{Q}|} - \int d\vec{x}_{e,1} \int d\vec{x}_{e,2} \phi_0^*(\vec{x}_{e,1}, \vec{x}_{e,2}; \vec{R}) \times \sum_{j=1}^2 \sum_{i=1}^2 \frac{e^2}{4\pi\epsilon_0 |\vec{x}_{e,j} + (-)^i (\vec{R}/2 + \zeta/2 \hat{Q})|} \times \phi_0(\vec{x}_{e,1}, \vec{x}_{e,2}; \vec{R} + s \hat{Q}). \quad (48)$$

It is worthwhile to note that, as already written in equation (47), $U(\zeta \hat{Q}, \vec{R}, s \hat{Q})$ is a function of ζ , R , s , and η only: $U(\zeta, R, s, \eta)$.

Considering the exemplificative character of the present calculations, it is not pointless to use a very crude approximation of the electronic wavefunction $\phi_0(\vec{x}_{e,1}, \vec{x}_{e,2}; \vec{R})$, namely its simplest MO-LCAO form [31]:

$$\phi_0(r_{A1}, r_{B1}, r_{A2}, r_{B2}; R) = \frac{1}{2 + 2I(R)} \times (\psi_{1s}(r_{A1}) + \psi_{1s}(r_{B1}))(\psi_{1s}(r_{A2}) + \psi_{1s}(r_{B2})), \quad (49)$$

with $r_{A1(2)} = |\vec{R}/2 + \vec{x}_{e,1(2)}|$, $r_{B1(2)} = |\vec{R}/2 - \vec{x}_{e,1(2)}|$, $I(R)$ being the overlap integral, and ψ_{1s} being a 1s Slater-type orbital [31]:

$$\psi_{1s}(r) = \frac{1}{\pi^{1/2}} \left(\frac{Z^*}{a_0}\right)^{3/2} \exp\left(-\frac{Z^* r}{a_0}\right), \quad (50)$$

where a_0 represents the Bohr radius and $Z^* = 1.197$. After some straightforward algebraic manipulations, one writes a MO-LCAO expression for $f(s, R, \eta)$:

$$f(s, R, \eta) = \left(\frac{I(s/2) + I(l)}{1 + I(R)}\right)^2, \quad (51)$$

where $l = \sqrt{R^2 + s^2/4 + s\eta R}$, and $I(x)$, the so-called overlap integral [32], reads

$$I(x) = \exp\left(-\frac{Z^* x}{a_0}\right) \left[1 + \frac{Z^* x}{a_0} + \frac{1}{3} \left(\frac{Z^* x}{a_0}\right)^2\right]. \quad (52)$$

As for the intra-molecular potential function U , the MO-LCAO expression reads

$$U(\zeta \hat{Q}, \vec{R}, s \hat{Q}) = \frac{e^2}{4\pi\epsilon_0} \frac{I(s/2) + I(l)}{(1 + I(R))^2} \left\{ \frac{I(s/2) + I(l)}{|\vec{R} + \zeta \hat{Q}|} - \frac{2Z^*}{a_0} \left[g\left(\frac{\zeta}{2} \hat{Q} + \vec{R}, \left(\frac{\zeta}{2} + \frac{s}{2}\right) \hat{Q} + \vec{R}\right) + g\left(\frac{\zeta}{2} \hat{Q}, \left(\frac{\zeta}{2} - \frac{s}{2}\right) \hat{Q}\right) + g\left(\frac{\zeta}{2} \hat{Q} + \vec{R}, \left(\frac{\zeta}{2} - \frac{s}{2}\right) \hat{Q}\right) + g\left(\frac{\zeta}{2} \hat{Q}, \left(\frac{\zeta}{2} + \frac{s}{2}\right) \hat{Q} + \vec{R}\right) \right] \right\}, \quad (53)$$

where $g(\vec{x}, \vec{y})$ is a three-centre Slater-type integral, and depends only on x , y and $\hat{x} \cdot \hat{y}$:

$$g(\vec{x}, \vec{y}) = \frac{1}{\pi} \left(\frac{Z^*}{a_0}\right)^2 \int d\vec{r} r^{-1} \times \exp\left[-\frac{Z^*}{a_0} (|\vec{r} + \vec{x}| + |\vec{r} + \vec{y}|)\right] \leq g(0, 0), \quad (54)$$

while $g(0, 0) = 1$ and represents the limit of $R^{-1} - J(R)$ ($J(R)$ being the well-known Coulomb integral [32]) for R going to zero.

Despite the simplicity of the LCAO orbitals in equations (49) and (50), the combined implementation of equations (47) and (53) is a tremendous numerical task since a six-dimensional integration is required for every s value. However, we have discovered (after some careful checks) that in our system equation (16) can be safely approximated by

$$\tilde{F}_1(s, \hat{Q}) \simeq i \tilde{F}_0^{(\text{st,cm})}(s) \int \chi_0^{(0)*}(\vec{R}) \chi_0^{(0)}(\vec{R} + s \hat{Q}) \times \langle \phi_0 | \int_0^s d\zeta [V(\vec{R} + \zeta \hat{Q}, \vec{x}_{e,1}, \vec{x}_{e,2}) - V(\vec{R} + s \hat{Q}, \vec{x}_{e,1}, \vec{x}_{e,2})] | \phi_0 \rangle f(s \hat{Q}, \vec{R}) d\vec{R}, \quad (55)$$

which, making use of equations (10) and (21), can be more easily evaluated. Numerical results for $\tilde{F}_0(s)$ and $\tilde{F}_1(s)$ making use of the MO-LCAO approximation are reported in figures 1 and 2, respectively, always in the case of $\langle \vec{V}^2 \rangle = 0$. In addition their Fourier transforms, $F_0(y)$ and $F_1(y)$, are plotted in figures 3 and 4, respectively.

4. Discussion of the H₂ calculation and conclusions

The calculation results for the asymptotic part of the response function, $F_0(y)$, evaluated with and without the inclusion of the electronic degrees of freedom, deserve little comment: the electronic term $f(s, R, \eta)$ acts like a small damping factor on $\tilde{F}_0(s)$ (see figure 1), and this appears, after Fourier transforming, as a sort of convolution in the y -space for a

modest broadening function (see figure 3). The physical meaning of this effect is not difficult to explain: the nuclear displacement, s , induced by the neutron scattering process, gives rise to a perturbed electronic wavefunction, whose overlap with its unperturbed equivalent (reported in equation (45)), is slightly lower than the unity and decreases as s grows. This term has to be thought as additional to the standard overlap of the perturbed and unperturbed nuclear wavefunctions (written in equation (42)), i.e., as mentioned above, like a damping factor.

On the contrary the first GRS correction term needs a quite longer and detailed discussion, since the inclusion of the electronic degrees of freedom shows to play a relevant role. In figure 2, it is possible to fully appreciate the differences between $\tilde{F}_1(s)$ and $\tilde{F}_1^{(st)}(s)$: the former is broader and peaked at a slightly lower s value, but, above all, exhibits the opposite sign with respect to the latter. One might think of possible numerical errors in the implementation of equations (47) and (53), but this is not the case, since the following low- s limit is satisfied [33]:

$$\lim_{s \rightarrow 0} \tilde{F}_1(s) = iA\tilde{F}_0(s)s^3, \quad (56)$$

with $A = 1126.0 \text{ meV } \text{\AA}^{-2}$. Naturally the same low- s behaviour is observed in $\tilde{F}_1^{(st)}(s)$, with a slightly different value of A ($A = 938.1 \text{ meV } \text{\AA}^{-2}$), but exhibiting the same sign. Both functions are reported in the inset of figure 2. So different reasons have to be found in order to explain the large difference between the two final state effect terms. Another point which is worth considering is the degree of accuracy of the electronic LCAO wavefunction employed in the present study (see equations (49) and (50)). It might be considered slightly too coarse since it yields the following H_2 Morse parameters: $R_0 = 0.732 \text{ \AA}$ and $D = 3.47 \text{ eV}$, to be compared to the experimental ones: $R_0 = 0.742 \text{ \AA}$ and $D = 4.75 \text{ eV}$ [34]. However, making use of the aforementioned LCAO coarse parameters in the framework of equations (41) and (43), one obtains $F_1^{(st)}(y)$ which is quite similar to the more accurate one, in no way exhibiting the feature observed in $F_1(y)$ (see figure 4). Thus, it is possible to conclude that the large discrepancies between the two final state effect terms $\tilde{F}_1^{(st)}(s)$ and $\tilde{F}_1(s)$ (and consequently $F_1^{(st)}(y)$ and $F_1(y)$) have a genuine physical character. In addition, it is worthwhile to observe the widely used first term, $\tilde{F}_1^{(SG)}(s)$, of the final state effect corrections due to Sears [35] and Glyde [36]:

$$\tilde{F}_1^{(SG)}(s) = i\langle \nabla^2 V_{N,M}(R) \rangle \frac{s^3}{36} \tilde{F}_0(s). \quad (57)$$

This term has been evaluated using the Laplacian of the standard Morse potential ($R_0 = 0.742 \text{ \AA}$, $D = 4.75 \text{ eV}$, and $\alpha = 1.9407$), with the inclusion of no electronic degrees of freedom, and is reported in figure 2. In spite of being rigorously correct only in the limit of small s values, as seen in equation (56), for larger ones $\tilde{F}_1^{(SG)}(s)$ becomes closer to $\tilde{F}_1(s)$ than to $\tilde{F}_1^{(st)}(s)$, at least as far as the general functional trend is concerned.

In order to provide a practical example of the differences implied by the two calculation methods, we have also

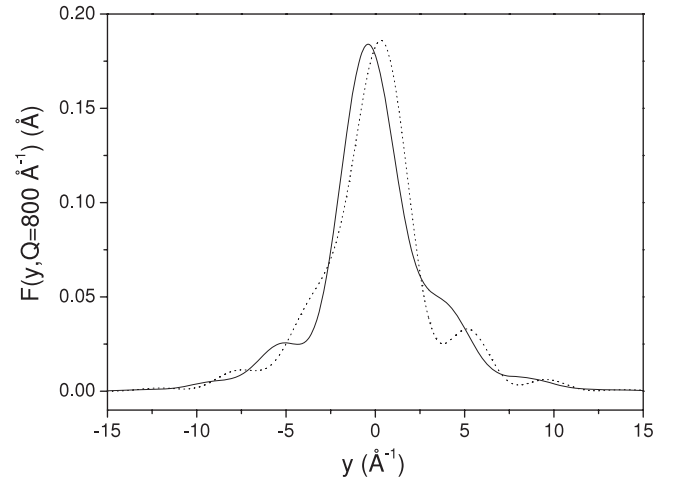


Figure 5. West-scaled response function for para-hydrogen vapour at $Q = 800 \text{ \AA}^{-1}$ in the framework of the standard approach (dotted line), and including the electronic degrees of freedom (full line). The two calculations are performed at low temperature (i.e. in the molecular roto-vibrational ground state), but include a centre-of-mass thermal broadening corresponding to $T = 20 \text{ K}$.

evaluated the full West-scaled response function (i.e. the Fourier transform of $\tilde{F}(s, \vec{Q})$, labelled $F(y, \vec{Q})$) for H_2 , since only this quantity is experimentally accessible via NCS. The calculation has been performed at a very high momentum transfer value, namely $Q = 800 \text{ \AA}^{-1}$, because exclusively the first final state effect term was available and, as shown in [26, 27], the asymptotic scattering regime is reached very slowly in the case of molecular hydrogen. We are aware that this selected momentum transfer value is presently not accessible by the existing NCS spectrometers; however the report on some pioneering low-resolution experiments with KeV neutrons [37] makes our calculations not too distant from a possible practical testability. The results are reported in figure 5 for two cases: in the framework of the standard approach, and including the electronic degrees of freedom. The differences between these two response functions are not large, but still clearly observable. It is worth noting that the two isotropic $F(y, Q)$ are both calculated in the para-hydrogen roto-vibrational ground state, but include a realistic centre-of-mass thermal broadening, as in equation (44), corresponding to a diluted vapour kept at a temperature of $T = 20 \text{ K}$.

In conclusion, we have clearly shown that the usual treatment of deep inelastic neutron scattering from molecular systems implicitly assumes the validity of the adiabatic approximation in both the initial and final molecular states. In addition, since this approximation has been recently questioned in order to explain some anomalous experimental results, we have proposed a calculation scheme able to get rid of the adiabatic assumption in the molecular states after the scattering process. This scheme generalizes the well-known Gersch–Rodríguez–Smith approach explicitly including the electronic degrees of freedom, and provides analytical formulae for the asymptotic response function and for the first final state effect correction. In order to understand the physical meaning of these two expressions, a practical calculation has

been performed on the simplest existing molecule: H₂, making use of approximate Morse potential nuclear wavefunctions and LCAO electronic orbitals. Results have come out of particular interest, showing an asymptotic term very close to the standard one, but slightly broadened because of the perturbation of the electronic wavefunction induced by the neutron scattering process via a non-adiabatic mechanism. On the contrary, the first final state effect terms (those proportional to the inverse of the momentum transfer), evaluated according to the Gersch–Rodriguez–Smith approach, exhibit large mutual discrepancies if they are evaluated using the semi-empirical internuclear potential (e.g. the Morse potential) or including electronic orbitals and Coulomb interactions. This fact, which surely deserves further clarification in future studies, suggests at the moment some caution in the use of the Gersch–Rodriguez–Smith approach in molecular systems like in [18]. In addition, keeping in mind the results reported in figure 2, it is not impossible to argue that the practical success of the correction method due to Sears and Glyde (currently used in almost all the NCS experiments [1]) is actually based on the role of the electronic degrees of freedom in neutron Compton scattering. Last but not least, it is important to stress that the present study, although originated by the proposed non-Born–Oppenheimer mechanism devised to explain anomalous NCS, is not directly related to this problem. The reason for this disconnection is simple: the aforementioned mechanism is based on the existence of isolated peaks (i.e. not following the exact West scaling) caused by the excitation of distinct electronic levels. This electronic fine structure is indeed contained in our model of equation (12), but, in order to be accurately reproduced, many terms of the Gersch–Rodriguez–Smith expansion in equation (13) are needed. Unfortunately at the moment only two terms are explicitly available. From a more physical point of view it is possible to observe that treating the response function through the Gersch–Rodriguez–Smith expansion (up to the second term), one implicitly assumes that nuclear recoil is so quick that even electrons are almost ‘frozen’ in their initial positions (we say ‘almost’ because the first correction to this purely asymptotic behaviour is actually included). Electronic transitions are indeed possible (since the internuclear distance changes while the electronic positions are practically ‘frozen’), but the overall effect looks very weak because Q is so large that even the electronic scattering features coalesce in a single peak in the y space. However, this scenario is still very distant from the eVS/VESUVIO regime [38] ($30 \text{ \AA}^{-1} < Q < 200 \text{ \AA}^{-1}$), where discrete electronic excitations could occur, well separated from the main H recoil peak.

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