

# Towards a covariance matrix of CAB model parameters for H(H<sub>2</sub>O)

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**Abstract.** Preliminary results on the uncertainties of hydrogen into light water thermal scattering law of the CAB model are presented. It was done through a coupling between the nuclear data code CONRAD and the molecular dynamic simulations code GROMACS. The Generalized Least Square method was used to adjust the model parameters on evaluated data and generate covariance matrices between the CAB model parameters.

## 1. Introduction

Below an incident neutron energy of approximately 5 (eV), the chemical binding of hydrogen in the light water molecule has a sizable impact on the neutron scattering process.

The double differential cross section of incident neutrons with energy  $E$  and direction  $\Omega$ , and secondary energy  $E'$  and direction  $\Omega'$  is expressed as:

$$\frac{d^2\sigma}{d\Omega dE}(E \rightarrow E', \Omega \rightarrow \Omega') = \frac{\sigma_b}{4\pi kT} \sqrt{\frac{E'}{E}} e^{-\beta} S(\alpha, \beta) \quad (1)$$

The thermal scattering function  $S(\alpha, \beta)$  depends on the dimensionless momentum change  $\alpha$  and the dimensionless energy change  $\beta$ :

$$\alpha = \frac{E' + E - 2\sqrt{E'E}\cos\theta}{AkT} \quad (2)$$

$$\beta = \frac{E' - E}{kT} \quad (3)$$

where  $\sigma_b$  is the characteristic bound cross section,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $A$  is the ratio between the scattering target mass and the neutron mass and  $\theta$  is the scattering angle in the laboratory system.

An integration of (1) over all secondary energies and solid angles gives an expression to obtain the elastic cross section from  $S(\alpha, \beta)$ :

$$\sigma(E) = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} \frac{d^2\sigma}{d\Omega dE} dE'. \quad (4)$$

## 2. Models to obtain the frequency spectrum of H into H<sub>2</sub>O

The scattering function  $S(\alpha, \beta)$  is processed with the LEAPR module of the code NJOY [1]. The frequency spectrum of hydrogen into light water defines the

excitation states of the material. It is computed in the LEAPR module as a convolution of three components: a continuous spectrum that models the intermolecular vibrations, a molecular translation that models the translation of the water molecule as free gas or diffusion and discrete oscillators which describe the intramolecular vibrations (bending and stretching modes).

We will describe two models that produce the frequency spectrum of hydrogen into light water.

The first model, IKE model, was obtained by M. Mattes and J. Keinert from KIT institute [2]. It is based on experimental measures of the double differential cross section between 294 K and 550 K.

The second model, CAB model, was obtained by J.I. Marquez Damian from Centro Atomico Bariloche [3]. The density of states of H(H<sub>2</sub>O) is calculated with the molecular dynamic simulations code GROMACS [4]. The translational mode was replaced by the Egelstaff-Schofield's diffusion model [5], instead of a free gas model.

The frequency spectrum of H into H<sub>2</sub>O at 300 K is shown in Fig. 1 for both models. The translational mode is not presented in the plot.

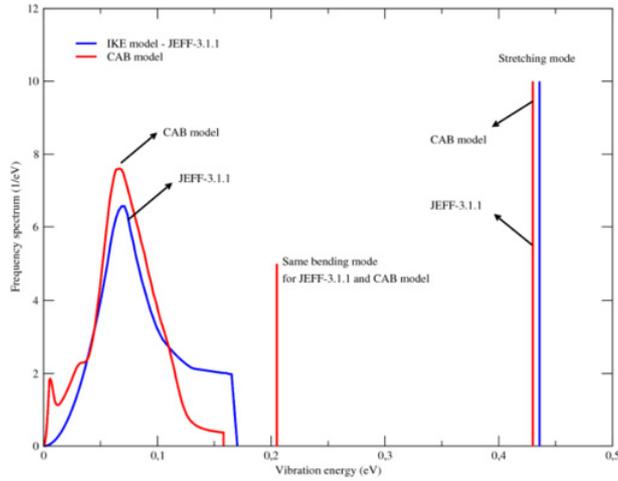
The total cross section calculated with CAB model and JEFF-3.1.1 model, together with experimental data [6–9], is presented in Fig. 2. The total cross section of JEFF-3.1.1 library reveals sizable discrepancies with experimental data for the cold neutron energy range ( $E < 10^{-4}$  eV).

## 3. Covariance generation methodology

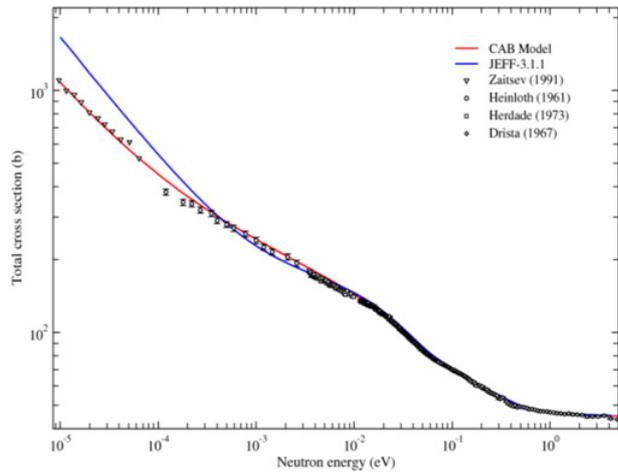
The quantification of the  $S(\alpha, \beta)$  function uncertainties involves the generation of the covariance matrix between the parameters involved in the CAB model.

The Generalized Least Square Method (GLS) in CONRAD code [10] provides the best estimate values of the model parameters in a fitting procedure with experimental data. The marginalization technique provides a tool to take into account the parameter uncertainties of systematic origin in the experiments [11]. These parameters, usually called as “nuisance”, refer to the

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**Figure 1.** Frequency spectrum of H(H<sub>2</sub>O) at 300K for CAB model and for JEFF-3.1.1 nuclear data library.



**Figure 2.** Light water total cross section at 300K for CAB model and for JEFF-3.1.1 nuclear data library.

normalization, the background and the sample thickness used in the experimental measures.

The final covariance matrix between all the model parameters is defined as follows:

$$\Sigma = \begin{pmatrix} \Sigma_{11} & \Sigma_{12} \\ \Sigma_{21} & \Sigma_{22} \end{pmatrix} \quad (5)$$

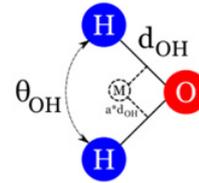
where each element of the symmetric matrix (5) is given by:

$$\begin{aligned} \Sigma_{11} &= M_X + (G_X^T G_X)^{-1} G_X^T G_\theta M_\theta G_\theta^T G_X (G_X^T G_X)^{-1} \\ \Sigma_{12} &= -(G_X^T G_X)^{-1} G_X^T G_\theta M_\theta = \Sigma_{21} \\ \Sigma_{22} &= M_\theta \end{aligned} \quad (6)$$

where  $M_X$  stands for the covariance matrix between the best-fit values of the model parameters, denoted as  $x$ , and  $M_\theta$  represents the covariance matrix between the nuisance parameters, denoted as  $\theta$ . The matrices  $G_X$  and  $G_\theta$  correspond to the derivatives of a certain quantity “ $z$ ” of interest with respect to the model and nuisance parameters

**Table 1.** Potential contribution to the light water potential TIP4P/2005f.

<b>Lennard-Jones potential</b>	$V_{L-j}(r_{ij}) = 4\epsilon_0 \left[ \left( \frac{\sigma_0}{r_i - r_j} \right)^{12} - \left( \frac{\sigma_0}{r_i - r_j} \right)^6 \right]$
<b>Coulomb potential</b>	$V_C(r_{ij}) = k \frac{q_i q_j}{r_{ij}}$
<b>Morse potential</b>	$V_M(r_{ij}) = D_{OH} [1 - e^{-\beta_{OH}(r_{OH} - d_{OH})}]^2$
<b>Harmonic angle potential</b>	$V_{H-O-H}(\theta_{ij}) = \frac{1}{2} k_\theta (\theta_{ij} - \theta_\theta)^2$
<b>Dummy atom position</b>	$a * d_{OH}$



respectively. They are defined as follow:

$$G_X = \begin{pmatrix} \frac{\partial z_1}{\partial x_1} & \cdots & \frac{\partial z_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial z_n}{\partial x_1} & \cdots & \frac{\partial z_n}{\partial x_n} \end{pmatrix}; G_\theta = \begin{pmatrix} \frac{\partial z_1}{\partial \theta_1} & \cdots & \frac{\partial z_1}{\partial \theta_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial z_n}{\partial \theta_1} & \cdots & \frac{\partial z_n}{\partial \theta_n} \end{pmatrix} \quad (7)$$

In the present study, the CAB model parameters correspond to the light water potential parameters used as input in the GROMACS code. A list of the contributions of the water potential TIP4P/2005f [12] as well as their respective parameters is reported in Table 1.

## 4. Results

### 4.1. Covariance matrix between CAB model parameters

The uncertainty and correlation matrix of the CAB model parameters was estimated with light water total cross section measurements from Refs. [6–9], covering a neutron energy range from  $10^{-5}$  eV to 10 eV. Measures of the average cosine of the scattering angle [13] were also included in the calculation.

It was done a two-steps calculation with CONRAD code, detailed as follows. Firstly, a fitting procedure is carried out, where the prior uncertainty on the model parameters is set to 1% and no correlation between them (the parameters are independent). Secondly, the auxiliary parameters (denoted as  $\theta$  parameters in Sect. 3) were marginalized. New posterior uncertainties and the correlation matrix between CAB model parameters are obtained.

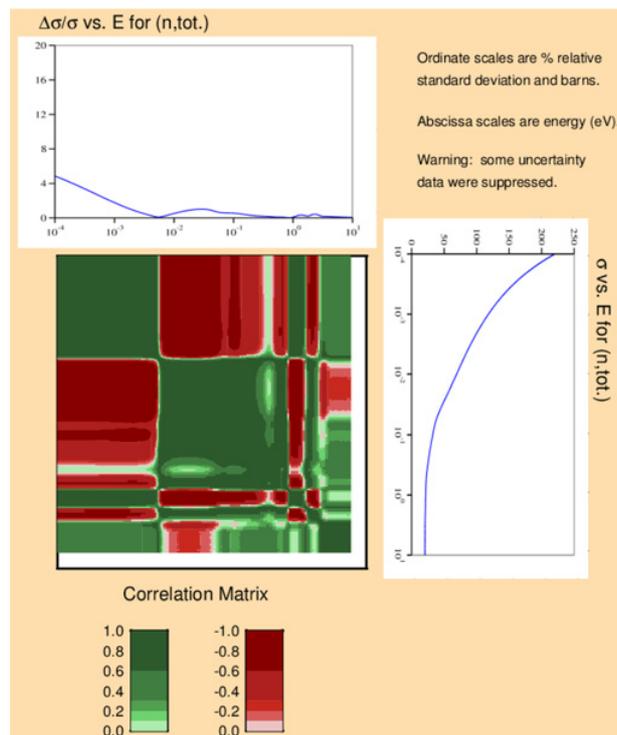
The posterior uncertainties and correlation matrix after the fit are reported in Table 2. This calculation step produces underestimated relative uncertainties on the model parameters. The results obtained after the marginalization are reported in Table 3. In this case, more realistic uncertainties and correlation matrix are obtained.

**Table 2.** Posterior uncertainties and correlation matrix between the CAB model parameters after the fitting step.

Parameter	Value	Results after the fit	
		Relative posterior uncertainty	Posterior correlation matrix
$\sigma_D$ [nm]	0,31644	0,6%	100 -17 25 63 -31 -14 19 -25 19
$\sigma_O$ [KJ/mol]	0,77491	0,8%	100 -33 -3 -10 -16 1 -26 -15
$q_H$ [e]	0,5564	0,7%	100 -51 -18 -13 12 -25 15
$d_{OH}$ [nm]	0,09419	0,7%	100 5 -14 -16 -5 5
$D_{OH}$ [KJ/mol]	432,58	0,8%	100 -31 15 -22 -2
$b_{OH}$ [1/nm]	22,87	0,7%	100 -7 -24 4
$\phi_0$ [°]	107,4	0,9%	100 -4 -9
$k_g$ [KJ/mol/rad <sup>2</sup> ]	367,81	0,8%	100 -10
$a$	0,13288	0,7%	100

**Table 3.** Posterior uncertainties and correlation matrix between the CAB model parameters after the marginalization step.

Parameter	Value	Results after the marginalization	
		Relative posterior uncertainty	Posterior correlation matrix
$\sigma_D$ [nm]	0,31644	2,3%	100 -77 93 69 33 -18 -64 83 -14
$\sigma_O$ [KJ/mol]	0,77491	14,6%	100 -71 -98 -85 53 97 -54 -32
$q_H$ [e]	0,5564	3,2%	100 59 28 -2 -60 81 -18
$d_{OH}$ [nm]	0,09419	6,3%	100 89 -63 -96 44 38
$D_{OH}$ [KJ/mol]	432,58	6,2%	100 -63 -88 6 57
$b_{OH}$ [1/nm]	22,87	4,2%	100 51 -11 -28
$\phi_0$ [°]	107,4	6,4%	100 -45 -49
$k_g$ [KJ/mol/rad <sup>2</sup> ]	367,81	3,8%	100 -14
$a$	0,13288	2,7%	100

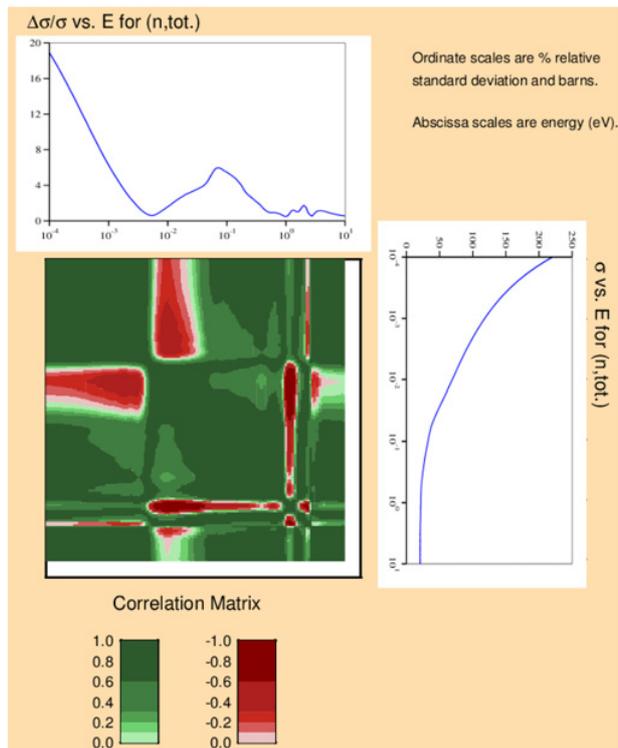


**Figure 3.** Relative uncertainties and covariance matrix for H(H<sub>2</sub>O) cross section after the fitting of CAB model parameters.

#### 4.2. Covariance matrix for light water total cross section

After obtaining a covariance matrix between the CAB model parameters uncertainties can be propagated to any given quantity of interest.

It was done a propagation of the parameters uncertainties to the elastic H(H<sub>2</sub>O) cross section. To point out differences between posterior results of the fitting and of the marginalization, the uncertainties and the covariance



**Figure 4.** Relative uncertainties and covariance matrix for H(H<sub>2</sub>O) cross section after the marginalization of the auxiliary parameters.

matrices of the elastic cross section were calculated in both cases.

Figure 3 shows the relative uncertainties and the covariance matrix of H(H<sub>2</sub>O) cross section after the fitting step. The small uncertainties on the CAB model parameters provide underestimated uncertainties for the elastic cross section.

Figure 4 shows the relative uncertainties and the covariance matrix of H(H<sub>2</sub>O) cross section after the marginalization step. Taking into account the parameter uncertainties of systematic origin, yields more realistic uncertainties on the elastic cross section.

### 5. Conclusions and future work

In the present work, preliminary covariance matrices of the CAB model parameters were obtained. A propagation of the parameters uncertainties was done to the elastic H(H<sub>2</sub>O) cross section, and realistic uncertainties were achieved.

It is intended to propagate the uncertainties of the CAB model H(H<sub>2</sub>O) thermal scattering law to integral experiments, using the Iteration Fission Probability algorithm (IFP) [14] in the Monte Carlo code TRIPOLI4.

### References

- [1] R.E. MacFarlane and A.C. Kahler, Nucl. Data Sheets **111**, 2729 (2010)
- [2] M. Mattes and J. Keinert, *Thermal Neutron Scattering Data for the moderator Materials H<sub>2</sub>O, D<sub>2</sub>O and ZrHx in ENDF-6 Format and as ACE Library for MCNP(x) Codes*. INDC (NDS)-0470 (2005)

- [3] J.I. Marquez Damian et al, Ann. Nucl. Ener. **65**, 280 (2014)
- [4] Van Der Spoel et al., Jour. of Computational Chem. **26**, 1701 (2005)
- [5] P.A. Egelstaff and P. Schofield, Nucl. Sci. Eng. **12**, 260 (1962)
- [6] K.N. Zaitsev et al., Sov. At. Energy **70**, 238 (1991)
- [7] K. Heinloth, Z. Phys. **163**, 218 (1961)
- [8] S.B. Herdade et al., Brazilian report to the I.N.D.C. No.2, p. 22 (1973)
- [9] M. Drista, A. Kostikas [X4# 20038003] (1967)
- [10] C. De Saint Jean et al., *CONRAD, a new software for nuclear data analysis*, Nuclear Energy Agency JEFFDOC-1142 (2006)
- [11] G. Noguere et al., Nucl. Sci. Eng. **172**, 164 (2012)
- [12] M.A. Gonzalez and J. Abascal, J. Chem. Phys. **135**, 224516 (2011)
- [13] J.R. Beyster, J.C. Young, J.M. Neill and W.R. Mowry, *Differential Neutron Scattering from Hydrogenous Materials - Annual Summary Report (GA-6295)*. General Atomics Technical Report (1965)
- [14] G. Truchet et al., Ann. Nucl. Ener. **85**, 17–25 (2015)