

¹ INS_IEP: A MATLAB package for fitting peaks of Inelastic Neutron Scattering data in spin cluster systems

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DOI: [10.xxxxxx/draft](https://doi.org/10.xxxxxx/draft)

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Submitted: 01 January 1970

Published: unpublished

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⁷ Summary

⁸ Inelastic neutron scattering (INS) is a spectroscopic technique that can be used to measure
⁹ the magnetic excitations in materials with interacting electron spins. For samples composed of
¹⁰ finite-size clusters of magnetic moment-carrying atoms, such as single ions or molecular-based
¹¹ magnets, INS experiments yield inelastic excitation with energies that correspond to the
¹² eigenvalues of the spin Hamiltonian of the material being studied. Fitting a model spin system
¹³ to these experimental eigenvalues can be formulated as an inverse eigenvalue problem (IEP),
¹⁴ where the matrix formed is the spin Hamiltonian operator of the sample molecule. Solving
¹⁵ this IEP is less computationally expensive than fitting the full INS data, so can be used as an
¹⁶ initial proxy for the full fitting problem. INS_IEP is a MATLAB package that uses deflated
¹⁷ numerical optimisation methods to systematically find multiple solutions to this IEP. The
¹⁸ package requires and is fully compatible with easyspin ([Stoll & Schweiger, 2006](#)), a package
¹⁹ for solving fitting problems in electron paramagnetic resonance (EPR).

²⁰ Statement of need

²¹ Neutrons are an excellent bulk probe of material properties since they carry no charge and
²² therefore penetrate deeply into matter. Neutrons also carry a quantum spin of a half, making
²³ them a sensitive probe of magnetism ([Squires, 2012](#)). Reactors and spallation sources with
²⁴ dedicated high-flux neutron sources serve the international research community with neutron
²⁵ scattering experiment capabilities for material research. Inelastic neutron scattering (INS) is
²⁶ one such experimental technique that can be used to study magnetism. In an INS experiment,
²⁷ a sample under investigation is irradiated with a beam of neutrons and the scattered neutron
²⁸ energy and momentum transfer are detected. For samples composed of finite-size clusters of
²⁹ magnetic moment-carrying atoms, such as single ions or molecular-based magnets, the detected
³⁰ neutron energy transfer gives direct access to the quantum spin excitations ([M. Baker & Mutka,](#)
³¹ [2012](#); [Furrer & Waldmann, 2013](#); "Spectroscopy Methods for Molecular Nanomagnets," [2014](#)).

³² The energy of such excitations relates to the energy difference between eigenvalues of the
³³ Hamiltonian matrix that describes the quantum spin dynamics of the compound in question.
³⁴ Single-ion and molecular-based magnets are studied as prototype components (quantum bits,
³⁵ sensors) for quantum technologies. INS can therefore provide crucial information concerning
³⁶ the precise quantum properties of such systems. However, to relate the INS experimental
³⁷ results to the Hamiltonian that describes quantum spin dynamics requires parameterisation of
³⁸ matrix elements such that a set of eigenvalues and eigenstates matching the experiment are
³⁹ determined. This situation is known as the inverse eigenvalue problem.

⁴⁰ To date, this problem is addressed in an iterative process where parameters of the Hamiltonian

41 are varied manually, often one at a time, and the resultant eigenvalues compared to the
 42 experimental values - each such iteration requires an eigendecomposition of the Hamiltonian
 43 matrix. INS_IEP presents an elegant solution to solving this problem, using algorithms to
 44 calculate multiple parameter sets that minimise the difference in eigenvalues, reducing the
 45 number of Hamiltonian matrix diagonalisations, and providing a more robust method to reliably
 46 extract an accurate spin Hamiltonian model from INS experimental data.

47 State of the Art

48 There currently exists fitting software designed to solve this problem, such as:

- 49 ■ SPECTRE ([A. T. Boothroyd, 1990](#)) uses the NAG Fortran Library for minimisation and
 50 matrix diagonalisation.
 51 ■ FOCUS ([Fabi, 1995](#)) uses Monte-Carlo and general quasi-Newton methods to find the
 52 parameters.
 53
 54 ■ PyCrystalField ([Scheie, 2021](#)) - fitting uses the SciPy minimize library.

55 All of these methods however only work for single ions (i.e. no exchange coupling) and only
 56 calculate one minimising system. INS_IEP however can fit INS data from samples with multiple
 57 spin centres, it can also find multiple minimising systems without multiple initial guesses to
 58 the parameter set.

59 Key Concepts

60 The Spin Hamiltonian

61 The Spin Hamiltonian, H , is an approximation of the Hamiltonian that uses spin coordinates
 62 instead of orbital coordinates, and is widely used to model data arising from many spectroscopy
 63 techniques ([Launay & Verdaguer, 2014](#)). It can be modeled as a linear combination of
 64 interaction terms; in this package we will use the zero field interaction, H_{ZFI} , and the
 65 electron-electron interaction, H_{EEI} :

$$H = H_{ZFI} + H_{EEI}.$$

66 Both of these terms can themselves be modelled as the linear sum of other basis matrices.
 67 The zero field interaction can be written as:

$$H_{ZFI} = \sum_{-k \leq q \leq k} B_k^q O_k^q$$

68 where the O_k^q are Stevens Operators ([Rudowicz & Chung, 2004](#)), and B_k^q the associated
 69 parameter. When there are multiple spin centres it is necessary to take Kronecker products of
 70 the operator with identity matrices of the appropriate for each other spin centre.

71 When there are multiple spin centres it is also necessary to include an electron-electron
 72 interaction term, H_{EEI} . This term will be the sum of interaction terms between each pair of
 73 spin centres:

$$H_{EEI} = - \sum_{i \neq j} J_{ij} S_i \cdot S_j$$

74 where S_i is the vector of spin operators $S_i = [S_x, S_y, S_z]$ for the i -th spin centre, and J_{ij} is
 75 the parameter to be found that represents the strength of interaction between the two spin
 76 centres. Note that in the isotropic case J can be thought of as a scalar value, but in the

77 anisotropic case will be a matrix where the off diagonals are skew symmetric (often the off
 78 diagonals are assumed to be zero). While the summation is in theory over all spin centre
 79 combinations, in practice many of these contributions will be negligible - often only the nearest
 80 neighbour interactions are significant.

81 It is important to mention that these matrix operators can be very large. The size is defined
 82 by the number of spin centres (n) and the spin (S_i) of each spin centre. The dimension of
 83 matrices is given by:

$$\prod_i^n (2S_i + 1).$$

84 The operators are however highly sparse, this means that it is possible to use eigensolvers that
 85 can take advantage of this sparsity.

86 Inverse Eigenvalue Problem

87 The INS experiments provide eigenvalues of the Spin Hamiltonian matrix of the sample, the
 88 task of calculating the matrix from the eigenvalues is an inverse eigenvalue problem:

89 Let $A(x)$ be the affine family of matrices,

$$A(x) = A_0 + \sum_{i=1}^{\ell} x_i A_i,$$

90 where $x \in \mathbb{R}^\ell$ and $A_0, \dots, A_\ell \in \mathbb{C}^{n \times n}$ are linearly independent Hermitian matrices, and denote
 91 the ordered eigenvalues of $A(x)$ as $\lambda_1(x) \leq \dots \leq \lambda_n(x)$. Then the least squares inverse
 92 eigenvalue problem (LSIEP) is to find the parameters $x \in \mathbb{R}^\ell$ that minimises

$$F(x) = \frac{1}{2} \|r(x)\|_2^2 = \frac{1}{2} \sum_{i=1}^m (\lambda_i(x) - \lambda_i^*)^2$$

93 where $\lambda_1^* \leq \dots \leq \lambda_m^*$ are the experimental eigenvalues (Chu & Golub, 2005). In the case of INS
 94 fitting the A_i basis matrices will be a combination of Stevens operators and electron-electron
 95 exchange terms. The IEP described above is formulated as an least squares problem because
 96 the number of eigenvalues that can be probed by INS experiments is often a small subset of
 97 the full spectrum. Due to the low temperatures that these experiments are performed at (can
 98 be as low as 1K) it is generally the smallest eigenvalues that are involved. Note also that since
 99 it is the energy difference between the eigenvalues that is probed we actually have to modify
 100 the IEP - either by adding an additional parameter (an identity matrix) that shifts the values
 101 of the eigenvalues, or by changing the above formula for F to directly sum the difference in
 102 eigenvalues thereby reducing the number of residual equations in $r(x)$ by one.

103 As far as we are aware this is the first time that the fitting of INS data has been explicitly
 104 formulated as an IEP. An advantage of this formulation is that there are explicit formulas for
 105 the derivatives of $r(x)$. The first derivative (Jacobian) is:

$$J_r(x) = \begin{pmatrix} q_1(x)^T A_1 q_1(x) & \dots & q_1(x)^T A_\ell q_1(x) \\ \vdots & \ddots & \vdots \\ q_m(x)^T A_1 q_m(x) & \dots & q_m(x)^T A_\ell q_m(x) \end{pmatrix},$$

106 and the second derivative (Hessian) is:

$$(H_r)_{ij} = 2 \sum_{k=1}^m (\lambda_k - \lambda_k^*) \sum_{\substack{t=1 \\ \lambda_t \neq \lambda_k}}^m \frac{(q_t^T A_i q_k)(q_t^T A_j q_k)}{\lambda_k - \lambda_t}.$$

¹⁰⁷ Another advantage is the number of constraints to fit is much smaller than fitting the spectrum
¹⁰⁸ itself, as it corresponds to fitting only the locations of the peaks of the spectrum.

¹⁰⁹ Methods

¹¹⁰ All of the methods used are iterative schemes of the form $x^{k+1} = x^k + p^k$ where the step p^k
¹¹¹ uniquely defines each algorithm:

- ¹¹² ■ Newton's method: $p^k = (J_r^T J_r + H_r r)^{-1} J_r^T r$ ([Nocedal & Wright, 2006](#))
- ¹¹³ ■ Gauss-Newton method: $p^k = (J_r^T J_r)^{-1} J_r^T r$ ([Nocedal & Wright, 2006](#))
- ¹¹⁴ ■ Lift and Projection Method: $p^k = B^{-1} J_r^T r$ ([Bloor Riley et al., 2025a](#))

¹¹⁵ Where the matrix B is the Gram matrix formed from the frobenius inner products of the basis
¹¹⁶ matrices: $B_{ij} = \langle A_i, A_j \rangle_F$. The Lift and Projection method is a Riemannian Gradient descent
¹¹⁷ method ([Bloor Riley et al., 2025a](#)), inspired by the Lift and Projection method ([Chu & Golub,](#)
¹¹⁸ [2005](#)), specifically designed for solving IEPs. In ([Bloor Riley et al., 2025a](#)) it is proven that the
¹¹⁹ method is a strictly descending algorithm, that is it reduces the value of the objective function
¹²⁰ every step. Both the deflated Gauss-Newton method and the Riemannian Gradient descent
¹²¹ Lift and Projection method are new methods designed for this package ([Bloor Riley et al.,](#)
¹²² [2025a, 2025b](#)).

¹²³ The m eigenvalues of required to calculate J_r are calculated using MATLAB's eigs command,
¹²⁴ which is an efficient method based on Krylov subspaces to calculate a small subset of the
¹²⁵ eigenvalues of the matrix. This is invaluable in this setting because computing the full set of
¹²⁶ eigenvalues by exact diagonalisation is in some cases infeasible ([Bloor Riley et al., 2025a](#)).

¹²⁷ Deflation

¹²⁸ The number of eigenvalues that can be probed via INS experiments varies depending on the
¹²⁹ equipment and sample in question, meaning that the fitting problem is often under or even
¹³⁰ over determined. The IEP is also highly nonlinear and due to the experimental nature of the
¹³¹ data may be ill-posed. One consequence of this is that the solution space may be very 'bumpy',
¹³² that is there may exist many local minimisers to the problem. For example in [Figure 1](#), there
¹³³ are clearly 4 distinct solutions (for more details see Example 1 and the file Example1_Mn12.m
¹³⁴ in the examples folder). We seek to solve the problem of multiple local minima by the use
¹³⁵ of Deflation, a numerical technique used to find multiple solutions to systems of equations
¹³⁶ ([Farrell et al., 2015](#)). Fortunately it is cheap to apply deflation for the above methods, it is
¹³⁷ simply a change to the length of the step - notably this means that the direction of each step
¹³⁸ does not change. It is proven in ([Bloor Riley et al., 2025b](#)) that the deflated methods will not
¹³⁹ converge to deflated points. The usual requirements still apply to the convergence of the new
¹⁴⁰ methods - that the initial guess is close enough to the new minimum, and that the Jacobian is
¹⁴¹ full rank in a neighbourhood around that minimum. The rate of convergence of the deflated
¹⁴² methods is also more complicated, although the number of iterations required to converge can
¹⁴³ go up with the number of deflations this is not a strict correlation, as can be seen in [Figure 2](#).

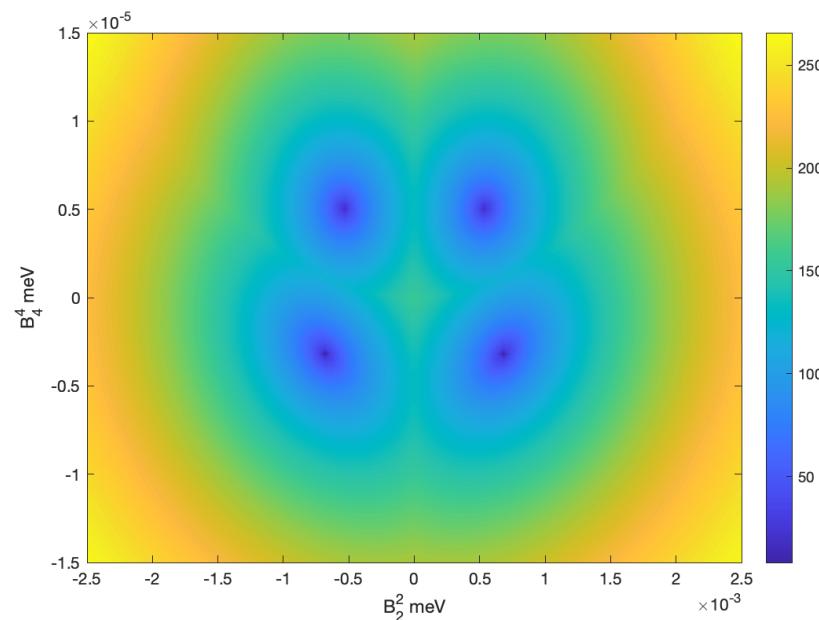


Figure 1: Contour plot of how F varies with the two parameters B_2^2 and B_4^4 for the molecule Mn_12 as described in Example 1. There are four locally minimising parameter pairs corresponding to the four blue regions

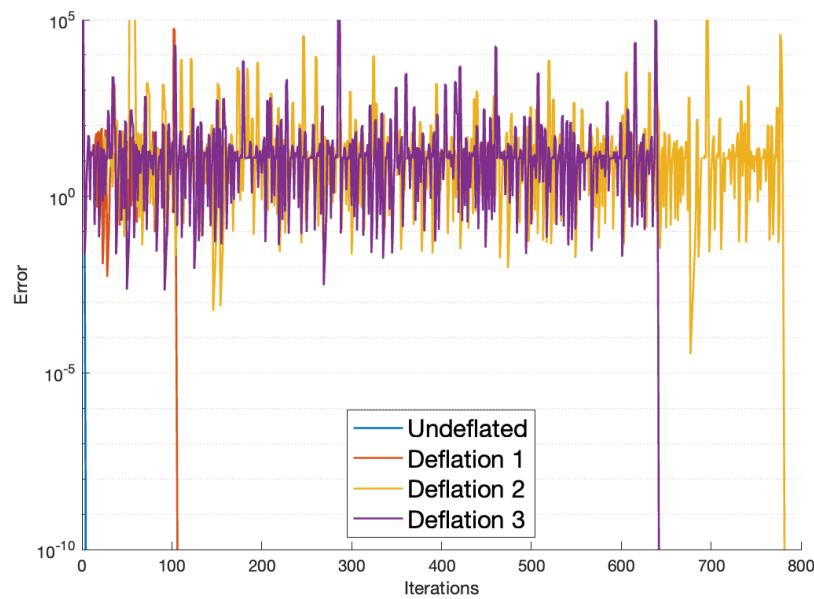


Figure 2: Comparison of the convergence behaviour for computing each solution in Example 1. The gradient of the lines as the method approaches the solution shows how the methods are quadratically convergent local to a minimum.

144 Examples

145 Example 1 - Mn12

146 The first example we will look at is Manganese-12-acetate. This is a well known example in the
 147 INS and magnetism community, as one of the first molecules that behaves like a nano-sized
 148 magnet with a molecular magnetic coercivity as well as its role in the research of quantum
 149 tunnelling of magnetisation (Friedman et al., 1996; Sessoli et al., 1993).

150 The Spin Hamiltonian of this system, using the giant spin approximation, can be represented
 151 as a 21×21 matrix modelled using 4 Stevens operators (Bircher et al., 2004):

$$H = B_2^0 O_2^0 + B_4^0 O_4^0 + B_2^2 O_2^2 + B_4^4 O_4^4 \in \mathbb{R}^{21 \times 21}$$

152 We utilise the same spin system syntax as easyspin, so to set up the problem we first set up
 153 the model, along with initial guesses for the parameters:

```
%One spin centre (because giant spin approximation)
Sys0.S=10;
%Four Stevens operators
Sys0.B2 = [-100,0,-1000,0,0];
Sys0.B4 = [-1,0,0,0,-1,0,0,0,0];
```

154 Then we input the experimental eigenvalues - these are typically shifted such that the smallest
 155 eigenvalue is zero - and define which parameters to fit. Note that all values given must be in
 156 gigahertz, so it may be useful to use conversions.

```
rcm = 29979.2458; meV = rcm*8.065; %Conversions values
%Input calculated eigenvalues:
Exp.ev = [0,0,1.24,1.24,2.3,2.3,3.18,3.18,3.91,3.91,4.5,4.5,
4.97,4.97,5.32,5.32,5.54,5.59,5.69,5.75,5.78].*meV;
%Note that these eigenvalues are simulated from the parameters given in [@bircher_trans]

%Vary all non zero parameters (no Fixed parameters):
Vary = Sys0;
```

157 Then all that is required is to call `INS_IEP` with these three inputs:

```
SysOut = INS_IEP(Sys0,Vary,Exp);
```

158 If we wish to find all four solutions as shown in Figure 1 then we use the additional option:

```
Opt.NDeflations = 4;
SysOut = INS_IEP(Sys0,Vary,Exp,Opt);
```

159 In this case `SysOut` will be an array of four spin structures each containing a distinct lo-
 160 cally optimal solution. It is possible to access information about the convergence of each
 161 deflation by using `SysOut.Output`. For example by utilising the iterates recorded, stored in
 162 `SysOut.Output.Iterates` it is possible to plot a graph of convergence, as can be seen in
 163 Figure 2. The Output structure also contains the value of F at the final point, as well as the
 164 number of iterations it took to get there.

165 A full list of options is provided in the help of `INS_IEP`.

166 Example 2 - Chromium(iii) Horseshoes

167 The second example concerns antiferro-magnetically coupled chain of six chromium(III) ions (M.
 168 L. Baker et al., 2011). Because there are multiple spin centres an electron-electron interaction
 169 term is required. The spin hamiltonian is a 4096×4096 matrix composed of two Stevens

170 operators and one interaction term, since it is known a priori that each spin centre will have
 171 the same value parameters we pin the parameters here, by setting the initial guess as the same
 172 value:

```
Sys0.S = [1.5 1.5 1.5 1.5 1.5 1.5];
Sys0.B2 = [1 0 -1 0 0;
            1 0 -1 0 0;
            1 0 -1 0 0;
            1 0 -1 0 0;
            1 0 -1 0 0;
            1 0 -1 0 0];
Sys0.J = [100,0,0,0,0,100,0,0,0,100,0,0,100,0,100];
Vary = Sys0;
Exp.ev = [0,0.355,0.457,0.497,1.576,1.577,1.592,1.629,1.632,
           2.97,2.98,3.002,3.004,3.01,3.038,3.821,3.824,3.827,
           3.837,3.856,3.879,3.888,3.895,3.903].*meV;
```

173 Note that only 24 eigenvalues were found experimentally, so this will form a partial LSIEP. To
 174 find the solution system is as simple as:

```
Opt.GradientTolerance = 1e-3; %Use additional stopping criterion.
SysOut= INS_IEP(Sys1,Vary1,Exp,Opt);
```

175 It is possible to find multiple minimising systems even if they do not make any sense physically,
 176 however due to the scaling of the problem a change in the default deflation parameters is
 177 necessary:

```
Opt = struct('NDeflations',5,'Sigma',1e-7,'StepTolerance',1e-3 );
SysOut= INS_IEP(Sys0,Vary,Exp,Opt);
```

178 The output contains five different spin systems that all have the same eigenvalues as input.
 179 Like in example one some of the minima found differ only by a sign change of the B_2^2 parameter,
 180 but all minima have the same exchange term.

181 Additional examples can be found in the Examples folder.

182 Note also that using mint ([M. L. Baker, 2022](#)), which is fully compatible with INS_IEP it is
 183 possible to simulate the INS spectrum of any calculated system - which can then be compared
 184 to the experimental spectrum. A description of how to do this can also be found in the
 185 examples folder.

186 Acknowledgements

187 We thank the reviewers Garrett Granroth and Chen Zhang for their help to improve the paper.
 188 ABR thanks the University of Manchester for a Dean's Doctoral Scholarship. MW thanks the
 189 Polish National Science Centre (SONATA-BIS-9), project no. 2019/34/E/ST1/00390, for the
 190 funding that supported some of this research.

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