



Computational Physics  
Master of Physics

# Magnetic interactions

## Solving Heisenberg Hamiltonian

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### 1 Introduction

This task is about computing magnetic configurations in two-dimensional (2D) materials for given interactions between magnetic moments. In order to illustrate the origin of magnetism in real materials, we will start with the simple example of the system consisting of two electrons in two different orbitals, which corresponds to the excited He atom (in the non-excited He atom both electrons occupy the same 1s orbital but with opposite spins). This example you may have seen in another master course, i.e. *Atom and Molecule Structure*. Electrons are labeled as "1" and "2" and orbitals as "a" and "b". The additional assumptions regarding the notation are: if two electrons occupy orbitals  $a$  and  $b$  with spins up, the resulting Slater determinant will be shortly written down as  $ab$ . If orbital  $a$  is occupied with spin up and orbital  $b$  with spin down, Slater determinant is written down as  $a\bar{b}$ . Similarly,  $\bar{a}b$  and  $\bar{a}\bar{b}$  correspond to Slater determinants where orbitals are occupied with spin down and spin up, and with both spins down, respectively.

If one calculates the matrix elements of the electronic Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{R}|} - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_2 - \vec{R}|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

in the basis set of the above explained Slater determinants, and then removes the constant diagonal contribution  $E_a + E_b$  [where  $E_\psi, \psi = a, b$ , satisfies the one-electron equation  $-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r} - \vec{R}|} \psi(\vec{r}) = E_\psi \psi(\vec{r})$ ], one will obtain following Hamiltonian matrix:

$$\mathcal{H} = \begin{bmatrix} K_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & K_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & K_{ab} & 0 \\ 0 & 0 & 0 & K_{ab} - J_{ab} \end{bmatrix}.$$

The order of the Slater determinants in this basis set is:  $|ab\rangle, |\bar{a}\bar{b}\rangle, |\bar{a}b\rangle$ , and  $|a\bar{b}\rangle$ . The parameters from the matrix are two-electron integrals:

$$K_{ab} = \frac{1}{4\pi\epsilon_0} \int \int a^*(1)b^*(2) \frac{e^2}{r_{12}} a(1)b(2) d^3\vec{r}_1 d^3\vec{r}_2 = \frac{e^2}{4\pi\epsilon_0} \int \int \frac{a^*(1)a(1)b^*(2)b(2)}{r_{12}} d^3\vec{r}_1 d^3\vec{r}_2,$$

$$J_{ab} = \frac{e^2}{4\pi\epsilon_0} \int \int \frac{\rho_a(1)\rho_b(2)}{r_{12}} d^3\vec{r}_1 d^3\vec{r}_2.$$

Obviously, the *direct integral*  $K_{ab}$  represents classical Coulomb interaction between two electrons localized in two different orbitals  $a$  and  $b$ . Contrary, another integral  $J_{ab}$  represents the exchange of electrons 1 and 2 between orbitals  $a$  and  $b$ . It does not exist in classical consideration, and is purely consequence of quantum mechanical treatment of the problem:

$$J_{ab} = \frac{1}{4\pi\epsilon_0} \int \int a^*(1)b^*(2) \frac{1}{r_{12}} a(2)b(1) d^3\vec{r}_1 d^3\vec{r}_2 = \frac{e^2}{4\pi\epsilon_0} \int \int \frac{a^*(1)b^*(2)a(2)b(1)}{r_{12}} d^3\vec{r}_1 d^3\vec{r}_2.$$

After calculating eigenvalues and eigenvectors of the Hamiltonian from relation  $\det(\mathcal{H} - \lambda \cdot I) = 0$  one obtains:

$$\lambda_1 = \lambda_2 = \lambda_3 = K_{ab} - J_{ab}, \text{ and } \lambda_4 = K_{ab} + J_{ab}$$

for eigenvalues, and

$$v_1 = |ab\rangle, v_2 = |\bar{a}\bar{b}\rangle, v_3 = \frac{1}{\sqrt{2}}(|\bar{a}\bar{b}\rangle + |\bar{a}b\rangle), \text{ and } v_4 = \frac{1}{\sqrt{2}}(|\bar{a}\bar{b}\rangle - |\bar{a}b\rangle)$$

for eigenvectors. Eigenvalues and eigenvectors 1, 2, and 3 correspond to the triplet state with total spin  $S = 1$  (parallel spins of two electrons), while 4th ones correspond to the singlet state with total spin  $S = 0$  (anti-parallel spins of two electrons). In case of electron exchange within a single atom, the integral  $J_{ab}$  is always positive, hence for single-atomic exchange the triplet state with parallel spins will always be lower in energy. This fact is the underlying microscopic basis for the Hund's first rule.

By having a closer look at the spectrum of the exact Hamiltonian  $\mathcal{H}$ , one can notice that its eigenvalues and eigenvectors can be reproduced by much simpler, phenomenological (quantum-mechanical) Heisenberg Hamiltonian:

$$\hat{\mathcal{H}}_{Heis.} = -2J_{ab}\hat{s}_1 \cdot \hat{s}_2,$$

by using  $\hat{s}_1 \cdot \hat{s}_2 = \hat{S}^2 - \hat{s}_1^2 - \hat{s}_2^2$ ;  $\hat{S}^2 = S(S+1)$ ,  $S = 0$  or  $1$ ; and  $\hat{s}_1^2 = \hat{s}_2^2 = \frac{1}{2} \cdot \frac{3}{2} = \frac{3}{4}$ .

This phenomenological Hamiltonian can be extended further to study the interaction between magnetic moments of ions<sup>1</sup> in a crystal. For this purpose

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<sup>1</sup>The magnetic moment of individual ions is "made" by unpaired electrons on that ion and in simplest consideration it is equal to  $N \cdot \frac{1}{2}$ , where  $N$  is the number of unpaired electrons on that ion. For example, the magnetic moment of  $\text{Cr}^{3+}$  is  $\frac{3}{2}$  due to  $N = 3$  unpaired electrons in  $d$ -shell.

it is convenient to consider the classical variant of the Heisenberg Hamiltonian, where magnetic moments on ions are classical 3D vectors (not operators), that is:

$$\mathcal{H}_{Heis.} = - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j.$$

At this point one should notice a remarkable fact - the origin of magnetic order in real materials lies in the quantum treatment of the Coulomb repulsion between electrons, which is a purely electrostatic interaction.

## 2 Magnetism in 2D materials

The previous section ended with a phenomenological *isotropic*<sup>2</sup> Heisenberg Hamiltonian, which describes magnetism in solids, however, this is sufficient only for bulk (3D) crystals. In case of 1D or 2D systems, long-range magnetic order can be stabilized only with anisotropy in magnetic interactions. In solid state physics, this is known as Mermin-Wagner theorem. The microscopic interaction that introduces the needed anisotropy is the spin-orbit coupling (SOC). It couples the spin of the electron to its orbital momentum, i.e. it couples the spin quantization axis to the real space  $\vec{r}$ , and hence "chooses" for a preferential direction/plane orthogonal to the direction, which is the very definition of anisotropy. Therefore, it is not surprising that the first synthesized magnetic 2D materials were CrI<sub>3</sub> and CrGeTe<sub>3</sub>, since I and Te are heavy atoms and consequently, host large SOC.

Practically, this means that with SOC included, each Cartesian component of each magnetic moment  $\vec{S}_i$  can interact with any component of the adjacent magnetic moment  $\vec{S}_j$ . In other words, Heisenberg exchange cannot be any more described with scalar  $J_{ij}$ , but with  $3 \times 3$  matrix  $[J]_{ij}$ . Finally, when inter- and intra-atomic exchange are formally separated, general Heisenberg Hamiltonian takes the form:

$$\mathcal{H}_{Heis.} = \sum_{i \neq j} \vec{S}_i [J]_{ij} \vec{S}_j + \sum_i \vec{S}_i [A]_{ii} \vec{S}_i.$$

If an external magnetic field is to be taken into consideration, one should add the Zeeman term  $H_B = -\mu_B g \vec{B} \cdot \sum \vec{S}_i$  to the above Hamiltonian. Here, your task is to study the general Heisenberg Hamiltonian for systems with  $\sim 100$  up to  $\sim 1000$  magnetic moments. In order to do so, you should minimize given general

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<sup>2</sup>The word *isotropic* refers to the fact that all Cartesian components ( $x, y, z$ ) of spins  $\vec{S}_{i,j}$  interact only pairwise ( $x$  with  $x$ ,  $y$  with  $y$ , and  $z$  with  $z$ ) and with equal strength  $J_{ij}$ .

Heisenberg Hamiltonian, under constraint that size of each magnetic moment is fixed to the value  $S$ . An illustration of how to do this will be given in the next section, on the example of an 8-site system and including only 1st nearest neighbors into the consideration.

### 3 Methodology

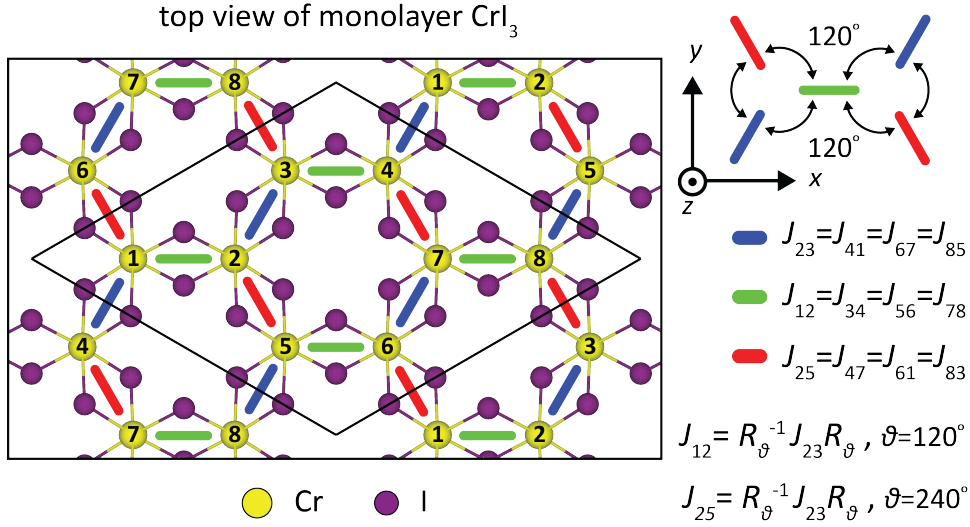


Figure 1: Bird-view of a two-dimensional  $\text{CrI}_3$  monolayer, with yellow and numbered Cr atoms, and purple I atoms.

In order to perform minimization of the Hamiltonian under constraint, we use Lagrange multipliers. Namely, we construct the function  $F$  from the Hamiltonian  $\mathcal{H}_{\text{Heis.}}$  and the function describing the given constraint, i.e.:

$$F = \sum_{i \neq j} \vec{S}_i [J]_{ij} \vec{S}_j + \sum_i \vec{S}_i [A]_{ii} \vec{S}_i - \sum_i \lambda_i \cdot (S^2 - \vec{S}_i \cdot \vec{S}_i).$$

Next step is to take derivatives with respect to every magnetic moment  $\vec{S}_i$  and take them equal to 0. From here on, we perform the procedure for the system shown in Fig. 1, including only 1st nearest neighbors and the intra-atomic exchange, and we obtain 8 vector-equations (each of them being 3 scalar equations actually):

$$\begin{aligned}
[J]_{16}\vec{S}_6 + [J]_{12}\vec{S}_2 + [J]_{14}\vec{S}_4 + 2[A]_{11}\vec{S}_1 &= -2\lambda_1\vec{S}_1, \\
[J]_{21}\vec{S}_1 + [J]_{23}\vec{S}_3 + [J]_{25}\vec{S}_5 + 2[A]_{22}\vec{S}_2 &= -2\lambda_2\vec{S}_2, \\
&\vdots \\
[J]_{87}\vec{S}_7 + [J]_{85}\vec{S}_5 + [J]_{83}\vec{S}_3 + 2[A]_{88}\vec{S}_8 &= -2\lambda_8\vec{S}_8,
\end{aligned}$$

It is straight-forward to generalize the procedure in case of  $N$  magnetic sites. One can see that this system of equations can be compactly written in a single matrix equation as:

$$\begin{aligned}
&\begin{bmatrix} 2[A]_{11} & [J]_{12} & 0 & [J]_{14} & 0 & [J]_{16} & 0 & 0 \\ [J]_{21} & 2[A]_{22} & [J]_{23} & 0 & [J]_{25} & 0 & 0 & 0 \\ 0 & [J]_{32} & 2[A]_{33} & [J]_{34} & 0 & 0 & 0 & [J]_{34} \\ [J]_{41} & 0 & [J]_{43} & 2[A]_{44} & 0 & 0 & [J]_{47} & 0 \\ 0 & [J]_{52} & 0 & 0 & 2[A]_{55} & [J]_{56} & 0 & [J]_{58} \\ [J]_{61} & 0 & 0 & 0 & [J]_{65} & 2[A]_{66} & [J]_{67} & 0 \\ 0 & 0 & 0 & [J]_{74} & 0 & [J]_{76} & 2[A]_{77} & [J]_{78} \\ 0 & 0 & [J]_{83} & 0 & [J]_{85} & 0 & [J]_{87} & 2[A]_{88} \end{bmatrix} \cdot \begin{bmatrix} \vec{S}_1 \\ \vec{S}_2 \\ \vec{S}_3 \\ \vec{S}_4 \\ \vec{S}_5 \\ \vec{S}_6 \\ \vec{S}_7 \\ \vec{S}_8 \end{bmatrix} \\
&= \\
&\begin{bmatrix} 2\lambda_1 \cdot I & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2\lambda_2 \cdot I & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\lambda_3 \cdot I & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\lambda_4 \cdot I & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\lambda_5 \cdot I & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\lambda_6 \cdot I & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2\lambda_7 \cdot I & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\lambda_8 \cdot I \end{bmatrix} \cdot \begin{bmatrix} \vec{S}_1 \\ \vec{S}_2 \\ \vec{S}_3 \\ \vec{S}_4 \\ \vec{S}_5 \\ \vec{S}_6 \\ \vec{S}_7 \\ \vec{S}_8 \end{bmatrix}.
\end{aligned}$$

In order to solve this system of equations we adopt the following iterative scheme:

1. We start by choosing initial spin configuration  $S$  in the form of a  $3N \times 1$  vector, and we multiply it from left by "large" Hamiltonian matrix ( $3N \times 3N$ ) consisting of  $A$ 's and  $J$ 's.
2. After obtaining the new  $3N \times 1$  vector, we split it into its  $3 \times 1$  constituents and calculate the norm of each of them. This calculated norm is divided by given value  $S$  - size of magnetic moment per site - and result is nothing but  $\lambda_i$ .

3. The  $3 \times 1$  constituents are then each divided by obtained  $\lambda_i$ . In this way it is ensured that each of the  $3 \times 1$  constituents are normed to S, before being connected back to the  $3N \times 1$  vector, which marks the spin configuration.
4. New spin configuration is finally obtained after "gluing" the pieces back together, and this new  $3N \times 1$  vector is again multiplied by the "large" Hamiltonian matrix from the left. The procedure is repeated until two successively obtained  $3N \times 1$  vectors are *negligibly* different (different up to a desired tolerance).

Described methodology is implemented in the shared MATLAB files. Together with these files, the  $3 \times 3$  input matrices are provided.

## 4 Tasks

1. Study the influence of the external magnetic field (vary its intensity, and direction) on the hysteresis of monolayer  $\text{CrX}_3$  ( $X = \text{I, Br}$ ). Compare results with the recent experimental observations [*Nature Electronics* **2**, 457–463 (2019)].
2. Study the spin configurations in case of magnetic frustration in the system ( $J_1 < 0$ ,  $J_2 \approx 0$ , and  $J_3 > 0$ ). Typical system hosting such a magnetic frustration are  $\text{NiX}_2$  monolayers ( $X = \text{I, Br}$ ). Study the influence of initial conditions on the resulting spin configurations. Compare the results to the recent publication in *Nature Communications* **11**, 5784 (2020).