
Theoretical Material Science: Electronic structure theory at
the computer

Dilute magnetic semiconductors

Prepared by Björn Bieniek, Lydia Nemeč and Volker Blum
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Some rules on expected documentation from this exercise.

The computational exercises are intended as “hands-on” experience with actual, numerical electronic structure theory. Our main goal is to fill some of the basic concepts with life for real systems.

This is a classroom-only exercise. We will look at the exercise together at the PC pool during the class on July 4. If you wish (and you are encouraged to do so), continue the steps on your own and let us discuss the results in class on July 11.

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1 Background

1.1 Dilute magnetic semiconductors

For a few years, there have been sketches of electronic devices (for instance, transistors) based on the electrons' spin instead of just their charge. The associated field is known as “spintronics” and producing workable devices along these lines would be really good indeed.

Now, nature seems to dictate that for semiconductor devices, semiconductor materials are a plus, and for spin-polarized electrons, ferromagnetic materials are not a bad idea either. It would be good if we had a material that is semiconducting and ferromagnetic at the same time, at room temperature, and that can be grown by conventional semiconductor technology. Then we could realize “spintronics”.

Unfortunately, as far as this author knows, we have no such material today. What is more fortunate is that all the necessary quantities are easily predictable from first principles theory. So if the experimentalists are too slow at guessing the right material, we should predict one for them.¹

One of the most popular candidate materials is $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, with $x \approx 2\%$ - 10% in most experiments. This material can be understood as a solid solution. The basic lattice is GaAs (zincblende), but with a fraction of the Ga atoms replaced by Mn.

1.2 Spin models

What we can explore for this exercise are two degrees of freedom:

1. Configurational
2. Spin

“Configurational” means that we get to choose where we place the Mn atoms in the crystal. We always use periodic supercells, but there are different possible Mn arrangements. We can try to suggest the one with the highest T_C . (Growing that exact structure in experiment is then a task for someone else.)

“Spin” means that we can legislate which spin sits on which Mn atom – “up” or “down”. It is important to note that in spin-polarized density functional theory as we use it here, there are really only two spin directions, up or down. We can thus calculate configurations that are purely “ferromagnetic” (all spins point up), purely “antiferromagnetic” (equally many up or down spins on the Mn atoms), or anything inbetween.

As a result, for a particular placement of Mn atoms on the lattice, we can compute different total energies E_{FM} , $E_{\text{AFM}}(\{S_i\})$, or anything inbetween. Note that there can be different ways to distribute spins on a lattice to give an overall antiferromagnetic state.

Since there are only up- and down-spins, the appropriate model to represent our energetics is not a Heisenberg model but an Ising-type model. We can postulate:

$$E(\{S_i\}) = -J \sum_{\langle i,j \rangle} S_i \cdot S_j \quad , \quad (1)$$

where we can formally choose $S_i = \pm 1$, and then move on to determine the parameter J from total energy calculations for different spin arrangements.

If we let the sum in Eq. (1) run over all possible inequivalent types of pairs, triplets, quadruplets etc. formed by the Mn atoms on the lattice, with different interaction parameters J_f for each such inequivalent “figure” f , this mapping on an Ising Hamiltonian would even be exact, known as a cluster expansion. The nearest-neighbour form above is just a common truncated interaction Hamiltonian used in the literature.

¹There are a few other small problems, such as whether a pure spin-polarized current can even be sustained, but we will leave such minor quibbles to the engineers.

Note that the spin on the Mn atoms is due to the spin splitting of the d levels on Mn, which is much larger than typical experimental temperatures. The moments located on each Mn atom themselves thus do not vanish with temperature, only their orientations can change. Our simple Ising model above will thus remain valid even at finite T .

1.3 Vegard's law

The change of the lattice parameter with the solute concentration x is often approximated by Vegard's law. It relates the lattice parameter of a solid solution to the concentration of the solute by a linear approximation. For example, consider the semiconductor compound $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. The relation between the constituent elements and their associated lattice parameters, a , is such that:

$$a_{\text{GaMnAs}} = x \cdot a_{\text{MnAs}} + (1 - x) \cdot a_{\text{GaAs}} \quad (2)$$

where x is the atomic concentration of manganese.

Often, Vegard's law is not a great approximation, but in this case and for small concentrations, experiments seem to indicate that it holds – see figure.

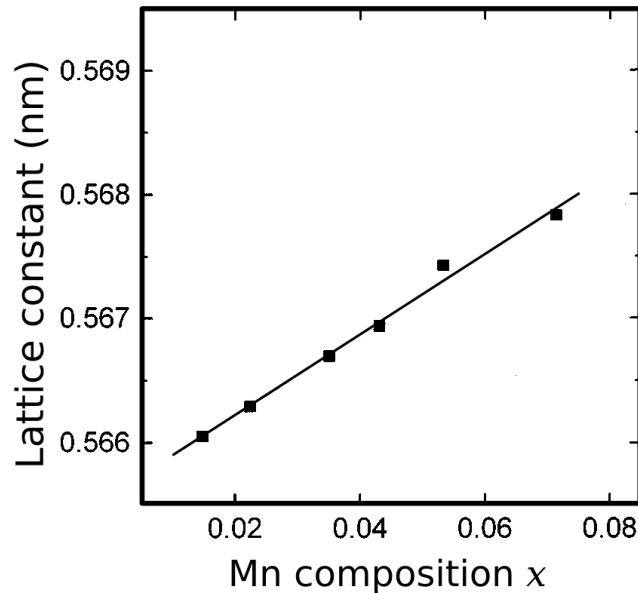


Figure 1: Vegard's law for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$: The lattice constant a is plotted versus Mn composition x in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ at room temperature. Plot taken from Ohno et al., APL 69, 363 (1996)

2 The exercise

Unlike in the last exercises, not every last detail will be scripted this time around. If you did the previous calculations, you already have the knowledge (and many of the basic input files) on which the present exercises can be based. This time, we “play” – use the input files and procedures from the last times as a model, and extend them as you see fit. Remember, in principle your quest is to predict a material which is as yet unknown, to anyone. Maybe you will find the first real room temperature ferromagnetic semiconductor arrangement in GaMnAs. If so, please let the authors of this exercise know.

As a quick reminder, here is (again) an overview of the most important pieces needed for FHI-aims at the “PC pool”.

- To run the code, create the necessary input files (`control.in` and `geometry.in`) in a working directory of your choice.
- For the present exercise, be sure to use more than one processor to run FHI-aims:

```
mpirun -np 2 aims.VERSION.mpi.x | tee calculation.out
```

As before, although you should not need it, there is a complete manual (pdf) for the FHI-aims code located in `/media/public/TFKP_2012/FHI-aims.pdf`.

Since some results have had to be precomputed for time reasons, also get the archive of precomputed solutions:

`/media/public/TFKP_2012/exercise13.solutions.tgz`

This archive can be unpacked in your own directory using the following command:

```
tar -zxf exercise13.solutions.tgz
```

2.1 Exercise 29a

This exercise is not yet computational.

The idea is to find out how many d levels there are in Mn, how many d electrons are left in a Mn^{3+} ion, and then use Hund’s rules to see how these electrons are distributed if there were no field whatsoever.

Next, this Mn ion lives in a real GaAs crystal, and thus in a tetrahedral environment. Remember that there is such a thing as crystal field splitting of the d levels, go to Wikipedia or elsewhere, and deduce what the appropriate splitting is for a tetrahedral environment. Then, assume that the spin splitting is much larger than the crystal field splitting (it is!) and draw a schematic level diagram.

In real GaMnAs, some of the d levels you have just drawn will hybridize with the As sp levels that surround them (someone has to do the bonding!), others will not (providing the spin). In fact, based on a *neutral* Mn atom (occupation $4s^23d^5$ in the atom), you will need the two s electrons and then two d electrons to hybridize. We will try to find out whether this simple picture is true.²

²As a side note: Even if this simple picture does turn out to be true in DFT-LDA, it is not *a priori* clear that the same thing will happen in real life. The description of the occupation of localized d states can be problematic in DFT-LDA, because LDA may underestimate the Coulomb repulsion due to a double occupation of the d orbitals. This Coulomb repulsion is described better by functionals which correct for self-interaction errors, for instance by including non-local exchange to some extent. We have included results from one such functional in exercise 29d), to give at least a rough idea of the expected trends.

2.2 Exercise 29b

In real life, we would now predict equilibrium geometries (lattice parameters, local atomic positions etc.) directly from first principles. Since we have no time, we will instead take lattice parameters from experiment, and keep all atoms fixed at their *ideal* lattice positions.

The idea of this exercise is to estimate how the lattice parameter should vary for GaMnAs alloys of varying composition (we will need those as input later).

2.3 Exercise 29c

Finally, a computation! The goal is to find out what the electronic level occupations of Mn even look like in this system, in DFT-LDA.

We do so by a “supercell” calculation, i.e. we assume a particular (and simple) supercell geometry with Ga and Mn atoms distributed on a lattice. To create a manageable structure, we choose the *conventional* (!) fcc cell formed by four Ga atoms and four As atoms, and replace one of them (e.g., the corner) by Mn. This gives us a total composition $\text{Ga}_3\text{Mn}_1\text{As}_4$, eight atoms.

A schematic picture of the structure is included.

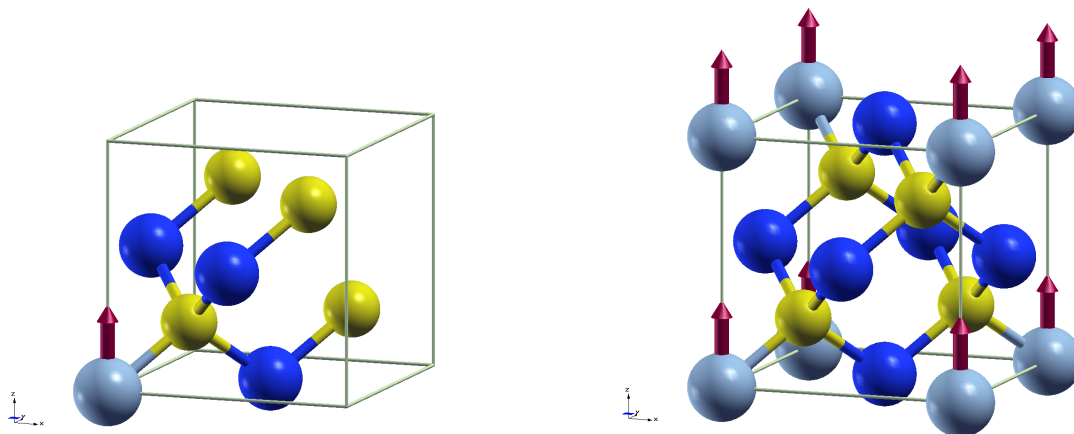


Figure 2: The cubic $(\text{Ga}_3\text{Mn}_1)\text{As}_4$ cell with 8 atoms. One Ga atom is replaced by an Mn. The left figure shows only the 8 atoms that are unique to the cubic cell. The right figure adds the other atoms on the corners and faces only for illustration.

- Create a `geometry.in` file for this structure as you did before, with the appropriate lattice parameter.
 - Remember that you could use the `atom_frac` keyword to specify atomic positions in units of the lattice vectors.
 - The single Mn atom in the structure needs to be equipped with an initial guess for the magnetic moment. Specifying:

```
initial_moment 4
```

immediately after that atom will do the trick.
- Create a `control.in` file for Ga, Mn, As with “light” species defaults, LDA as the exchange-correlation functional, and spin (the `spin collinear` keyword).
 - Use a dense enough k -grid - $4 \times 4 \times 4$ is on the low end.
 - The *total* DOS can be plotted as usual by:

```
output dos -30 0 1000 0.1
dos_kgrid_factors 5 5 5
```

- You also want the “projected density of states,” i.e., the fraction that is attributable to the atomic orbitals of any given atom. Use:

```
output species_proj_dos -30 0 1000 0.1
```

That should suffice to give you the required results. Two things:

The “projected density of states” onto a given atom is not a uniquely define thing. We here require a concept called “atoms in molecules”, and if there is more than one atom, there *is no unique way* to decide whether a given part of the electron density came from the angular momentum channels of one atom or of another.

We here use a concept called a “Mulliken analysis” which simply takes the Kohn-Sham levels and distributes the electrons in each state (at single-particle energy ϵ) into the atoms and angular momentum channels where the associated basis functions came from – a projection. Since basis functions overlap between different atoms, electrons are “evenly assigned” between them. This way of classifying is anything but unique and gives increasingly bad results as the basis set increases in size (because then, electrons on one atom can easily be represented by the basis functions coming from another atom).

With our settings and basis size the concept still works well on a qualitative level, but again, different schemes could be found.

In any event, based on the keywords above, the code produces files called

- KS_DOS_total.dat
- Mn.l_proj_dos_spin_up.dat
- Mn.l_proj_dos_spin_down.dat

The total DOS contains information for *both* spin channels. For the Mn files, this is the occupation of angular momentum channels on the atom for the up and down channels, separately. You are interested in the *d* channels ($l=2$), which is the fifth column. Read the header of either file if you are unsure.

All these densities of states can be plotted together using xmgrace (directly), do not try to use a pre-built script. If you plot the total spin up DOS, the total spin down DOS, the Mn spin up *d* DOS and the Mn spin down *d* DOS together as a function of energy, you will see which part of the Kohn-Sham density of states is derived from which atomic levels, approximately.

We also note that the `output species_proj_dos [...]` keywords already sums up all the contributions from every atom of a given element, so there is only one file for Ga instead of 3, etc. This is ok, as we do not need to see 3 Ga atoms separately here, anyway. We could, if you wanted to ... (ask).

(continued on next page for clarity)

There is some more information in the FHI-aims standard output if all went well. Look for the following section:

Performing Mulliken charge analysis on all atoms.

Full analysis (per state, per k-point, etc.) will NOT be written to separate file 'Mulliken.out'

This file can be requested by stating 'output mulliken' explicitly.

Summary of the per-atom charge analysis:

atom	electrons	charge	l=0	l=1	l=2
1	24.822252	0.177748	6.665034	12.486492	5.661639
2	33.311139	-0.311139	7.772708	15.407925	10.130506
3	30.644398	0.355602	7.137535	13.344343	10.162520
4	33.311139	-0.311139	7.772708	15.407925	10.130506
5	30.644398	0.355602	7.137535	13.344343	10.162520
6	33.311139	-0.311139	7.772708	15.407925	10.130506
7	30.644398	0.355602	7.137535	13.344343	10.162520
8	33.311139	-0.311139	7.772708	15.407925	10.130506
Total	250.000000	0.000000			

Summary of the per-atom spin analysis:

atom	spin	l=0	l=1	l=2	l=3
1	4.018188	0.105790	0.102621	3.810078	-0.000302
2	-0.049338	0.000128	-0.070500	0.021035	
3	0.059064	0.024862	0.034323	-0.000122	
4	-0.049338	0.000128	-0.070500	0.021035	
5	0.059064	0.024862	0.034323	-0.000122	
6	-0.049338	0.000128	-0.070500	0.021035	
7	0.059064	0.024862	0.034323	-0.000122	
8	-0.049338	0.000128	-0.070500	0.021035	
Total	3.998030				

This gives you integrated values for the spin and angular momentum occupations of each atom. How many d states are filled on Mn (total)? Given the residual spin per atom (given as $N_{\text{up}} - N_{\text{down}}$), how many spin down electrons are there?

Compare this count of d electrons to what was expected for the neutral atom! You will find a difference.

2.4 Exercise 29d

An 8-atom cell is not really dilute. We have therefore doubled the unit cell size in all directions and computed the properties of a more isolated Mn atom in a 64 atom cell. Since the computation would be too time-consuming, just look at the results and plot the various densities of states as in the previous exercise.

LDA results are good for total energies, but as you know, the energy levels are sometimes not particularly good. This can be seen by going to a more sophisticated functional that includes some screened exact exchange in its single-particle equations.

We have provided files both for the LDA and for the HSE06 functional for you.

Especially the HSE06 functional is interesting. Since there is actually a reasonable band gap in this functional, you can take the DOS and see where the top of the spin-up valence band is. You will see that it contains empty states – holes! In essence, the Mn atom fills up one more of its d orbitals than it has electrons for, and it gets the missing electrons from the top of the valence band. Thus, we create holes.

These “holes” are what mediates the ferromagnetic interaction between the (otherwise isolated) Mn atoms. The holes are extended, in contrast to the d states of a Mn atom, which are localized.

2.5 Exercise 29e

Well - if you read this document up to here, you should know what to do ...

2.6 Exercise 29f

This is the last tricky bit. For this exercise, you need supercell with *two* Mn atoms at least, so that you can create one ferromagnetic and one antiferromagnetic configuration.

If you use the same distribution of Mn atoms as before, that now makes a supercell that contains a total of 16 atoms.

Furthermore, this system has states at the Fermi level. You will need a good k grid, for instance $6 \times 6 \times 6$. (Better $12 \times 12 \times 12$, for the *entire* cell.)

For the FM version, just give *both* Mn atoms

```
initial_moment 4
```

```
in geometry.in.
```

For the AFM version, give one of them

```
initial_moment 4
```

```
and the other initial_moment -4
```

This will do to make sure that the final spin state (after self-consistency is reached) is either FM or AFM.

2.7 Exercise 29g

If you subtract the total energies of both calculations from one another, you will get a very small value. You can calculate the J parameter of an Ising model (but make sure you count the right number of Mn neighbour pairs per cell!) and then calculate T_c . What do you get?

2.8 Outlook (for a theorist)

For now, we have looked at a relatively large concentration of Mn atoms, where each atom has multiple nearest neighbours.

Alternatively, we could try to determine our J by looking at more dilute structures where we have only isolated Mn atom pairs, or, at least, only connected in one direction ... etc.

We have precomputed a 64-atom unit cell with an isolated Mn nearest-neighbour pair in (110) orientation for you, both FM and AFM. Take a look at the structure and the total energy. What is the ferromagnetic interaction strength between both atoms?

We have also precomputed a 64-atom unit cell with a chain of Mn nearest-neighbour pairs in the (100) direction, both FM and AFM. Again, take a look at the structure and at the total energies. What is the interaction strength this time?

Finally, there is a Mn pair with (220) connection vectors, both FM and AFM. Again, take a look at the structure and the total energy. What is the ferromagnetic interaction strength now?

The interesting question is this:

We could have considered any other arrangement of Mn atoms in the lattice. Indeed, the FM coupling between Mn atoms is much stronger along (say) the (110) or (210) directions than along the (100) direction.

So if one took an arrangement of Mn atoms with (110), (210) etc oriented connection vectors instead of our simple cubic arrangement of Mn atoms in a matrix (where the connection vectors are all (100)), we could possibly generate a much higher T_C .

And then, if our theory were exactly right, we could give that structure to someone versed in atomic-scale growth of semiconductor films and challenge them to grow that structure. Long shot ...but perhaps not entirely impossible.