

Ab initio studies of vacancy-impurity complexes in cubic and hexagonal diamond

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Advisor: Prof. Dr. Andreas Grüneis

Ab initio studies ...



Hello my name is Alejandro and I am currently working on my master thesis project entitled:

Ab initio studies of vacancy-impurity complexes in cubic and hexagonal diamond

The supervision of the project is conducted by Dr. Andreas Grueneis , head of group at the MPI for solid state research. We engaged in this project as a joint collaboration with the third physical institute of this University, which is led by Prof. Joerg Wrachtrup.

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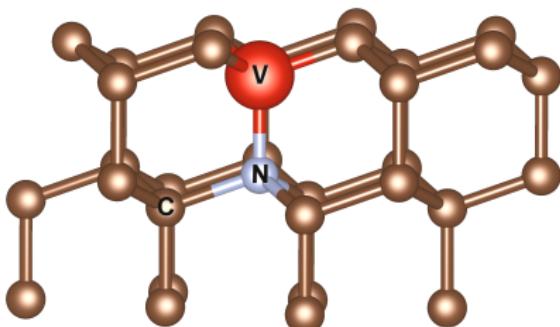
In the following we will provide some basic background in the field of vacancy-impurity complexes and we will quickly introduce some of the techniques used to model and calculate their electronic properties.

The main systems of this work will be introduced and we will finish by giving a quick outlook into the possible future directions that this research could be led into.

Aim and scope of the work

Aims and motivation

- Exploration of defect centres using state-of-the-art ab-initio theories.
- Benchmark ab initio theories with well-known experimental data.
- Systematic characterisation of defect fingerprints: ZFS, ZPL.
- Search for new defects with tailored properties which are useful for different applications.



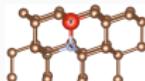
Ab initio studies ...

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Aims and motivation

- Exploration of defect centres using state-of-the-art ab initio theories.
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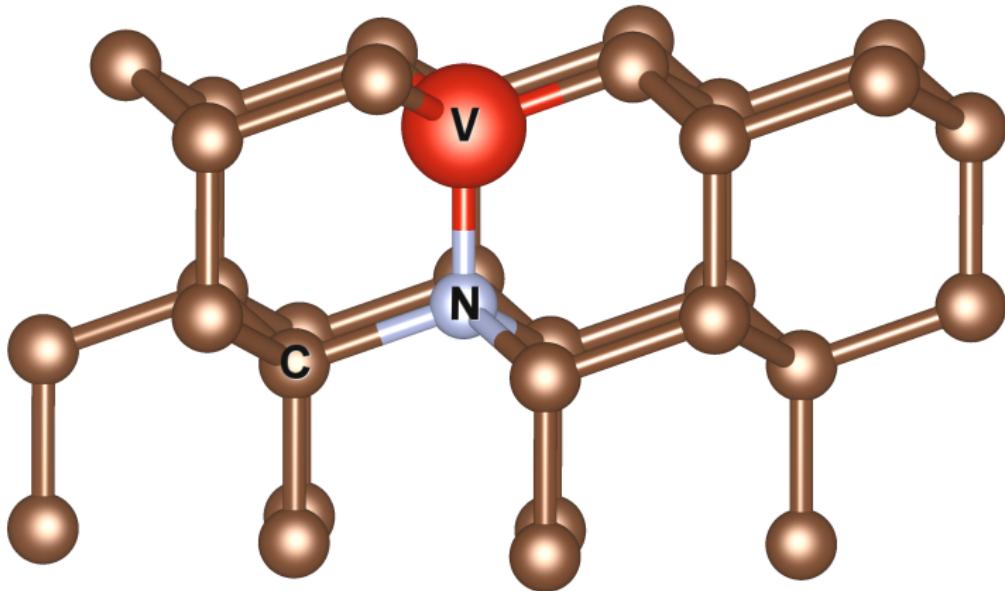
So the main aim of this work is to computationally treat electronic properties of defect centers in diamond using state-of-the-art ab initio theories.

Through this exploration we hope to recover many well-known experimentally verified quantities.

In order to do this we use several purely theoretical results to orient our calculations into the right direction. (e.g. Markus' Gruppentheorieberechnungen)

Introduction

Nitrogen Vacancy Centre in diamond (NV center)

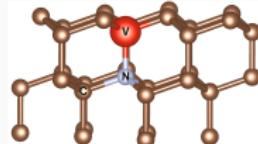


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└ Introduction

└ Nitrogen Vacancy Centre in diamond (NV center)



So let us just begin by firstly introducing the main actor in this story.

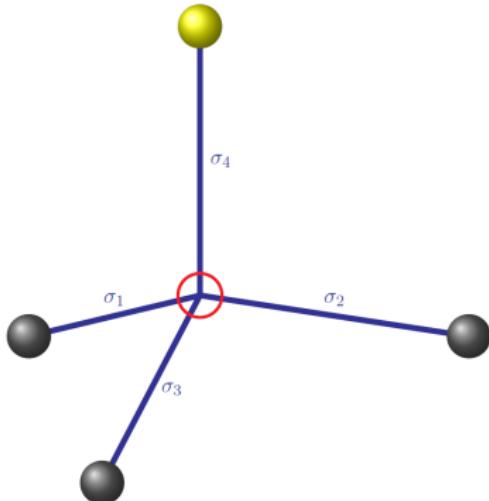
This is the Nitrogen vacancy impurity center in diamond, as most of you may already know. The big red region is a vacant carbon site and next to it lies a nitrogen atom.

This kind of defects has been researched now for almost 50 years.

However it was not until the late nineties when single negatively charged NV centres where found. This enabled the demonstration of photo stable single photon emitters, which is of course of huge importance for quantum optics.

The most notable and studied of the NV centers is the negatively charged one.

Nitrogen Vacancy Center (Dangling bonds)



- Model for the defect $4\ sp^3$ dangling bonds $\{\sigma_1, \dots, \sigma_4\}$
- Linear Combination of Atomic Orbitals (LCAO) to account for C_{3v} symmetry.
- In the case of NV^- we have $1\#C + 2 \times \#N + 1e = 6$ electrons.
- From σ_i we obtain 4 levels $a_1(1), a_1(2), e(1), e(2)$ classified according to their symmetry.

Basic level overview

Conduction Band

$e(1)$ ————— $e(2)$

$a_1(2)$ —————

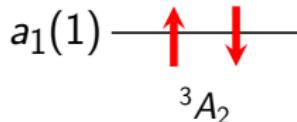
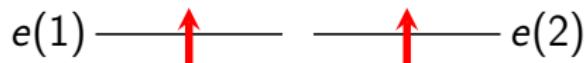
$a_1(1)$ —————

Valence Band



Basic level overview: Ground State

Conduction Band

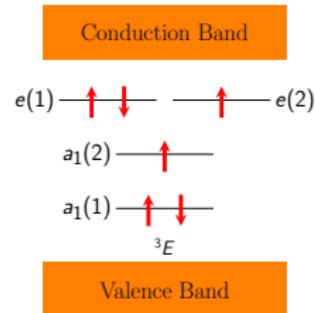
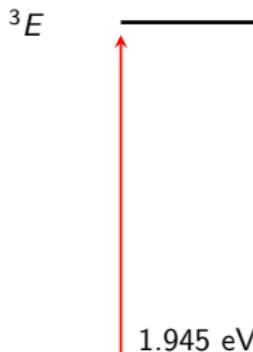


3A_2

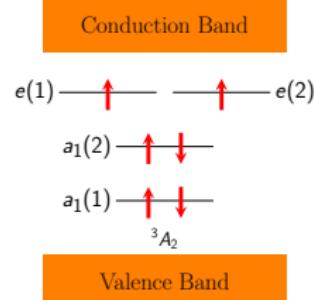
Valence Band



Triplets overview: NV⁻

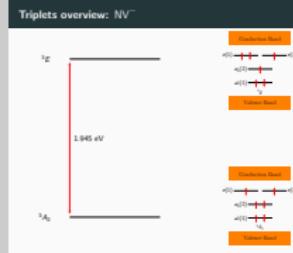


3A_2



Ab initio studies ...

└ Introduction

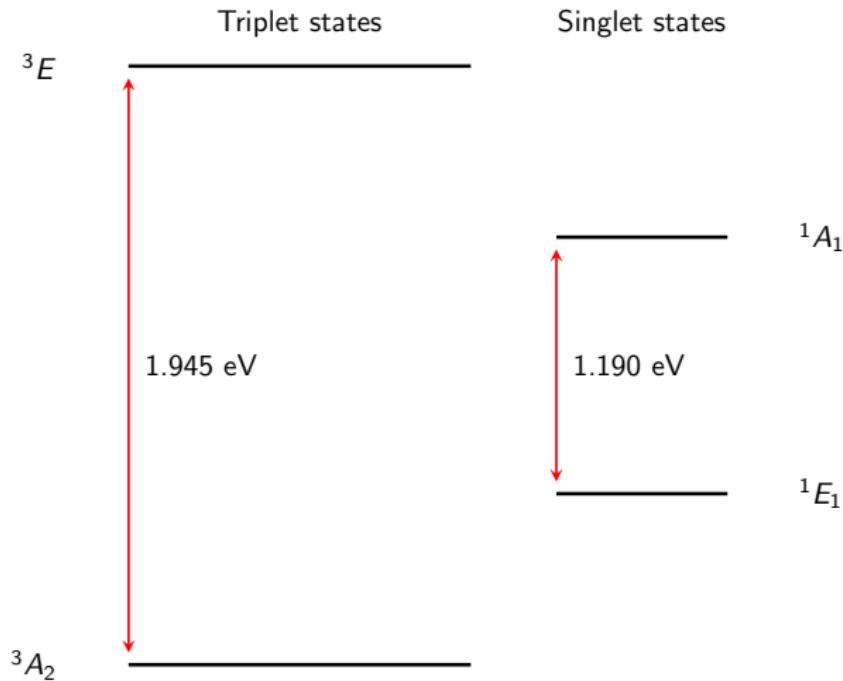
└ Triplets overview: NV⁻

If you have never heard of this defect before, you might be wondering how exactly the electrons in the solid body come into play. In the one particle picture of the problem it turns out that we can characterise very well these levels by the occupation of the valence states in the body.

In this picture we can associate to every state with an occupation of the topmost states. From this picture we can see that the total spin is one and the excitation happens through the promotion of one electron in the level a_1 into one of the degenerated e levels. This without incurring in a spin flip process.

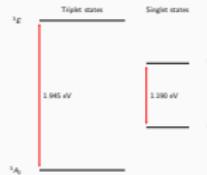
This we should also find in our calculations.

Main level overview: NV⁻



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└ Introduction

└ Main level overview: NV⁻Main level overview: NV⁻

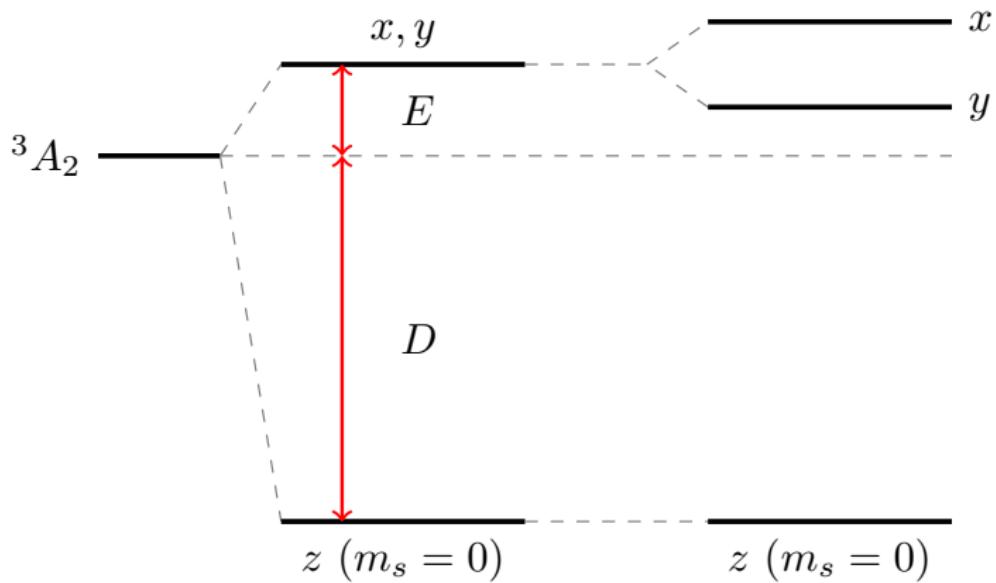
To explain fluorescence experiments it is essential to have a picture of the electronic and vibronic states of a defected diamond sample. Theoretical models using a *Linear combination of atomic orbitals* (LCAO) give rise to a good prediction of the Spin multiplicity and triplet energy levels of the negative NV center.

From the interplay of theory and experiments arises this electronic level scheme. On the one hand we encounter two stable triplet levels, where one of them is the ground state of the defect. Between them lie two metastable singlet states, which will play an essential role for applications of the defect levels.

Zero Field Splitting (ZFS)

$\hat{\mathbf{S}}^t \mathbf{D} \hat{\mathbf{S}}$

Zeeman/strain



REVISE E AND D



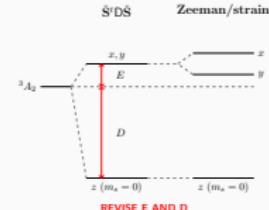
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└ Introduction

└ Zero Field Splitting (ZFS)

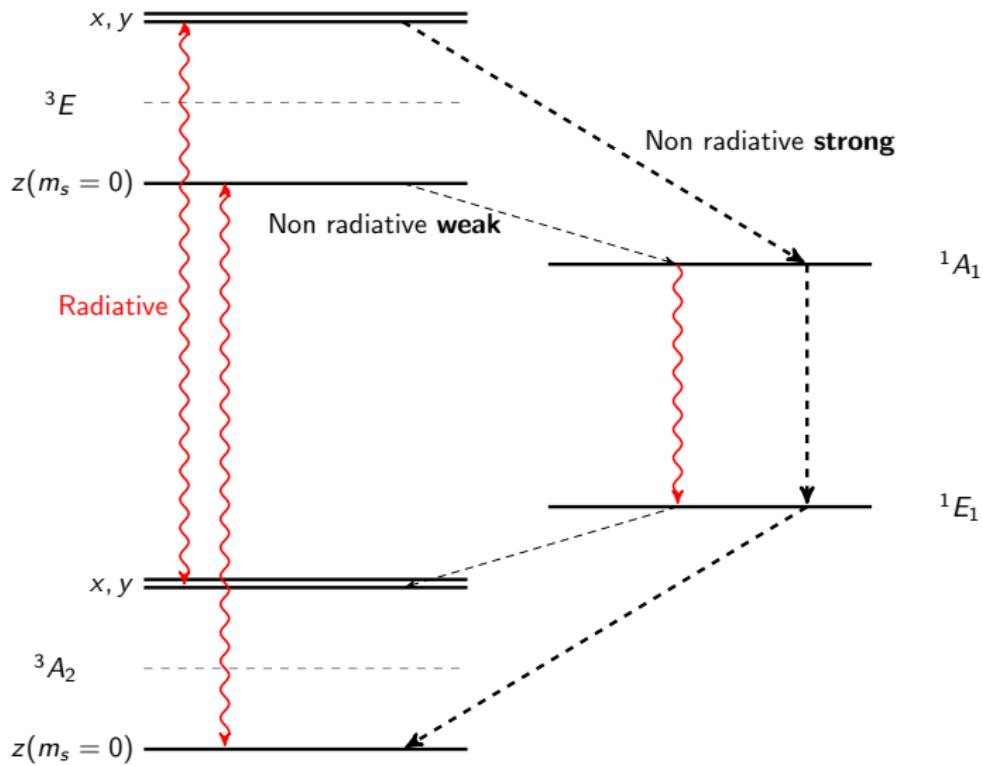


Another important aim of our project is to calculate correctly the zero field splitting of the energy levels.

In this case we are interested in the splitting that arises from the Spin-Spin interaction of the electrons. This splits into up to three levels the triplet state. This splitting is characterised by two parameters, E and D .

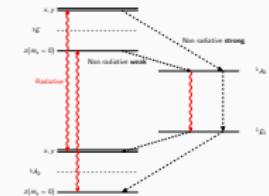
The splitting also arises through strain of the material and Zeeman splitting.

Transitions overview: NV⁻



Ab initio studies ...

└ Introduction

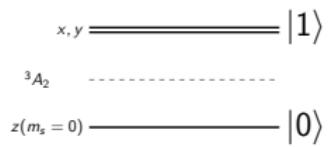
└ Transitions overview: NV⁻Transitions overview: NV⁻

One of the main uses that these levels have in common applications of the NV center is best understood by the following diagram. In it we see the triplets on the left with a splitting in place and the singlet states on the right.

To understand this diagram imagine that the level population of the $m_s = 0$ in the 3A_2 state is much higher than the x, y split states of the same state. If we radiate with the right frequency of the energy difference between both triplet states, then a non radiative transition brings the system into the singlet state, where a radiative transition happens. In both possible cases, radiation is produced, therefore a detector would take a hold of this radiation.

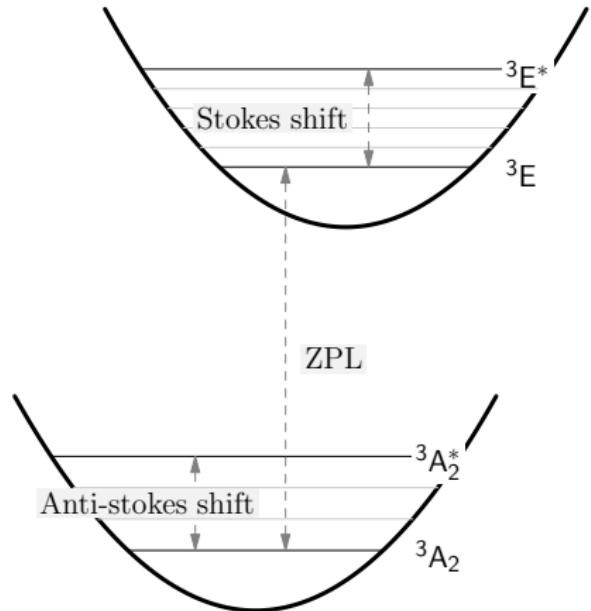
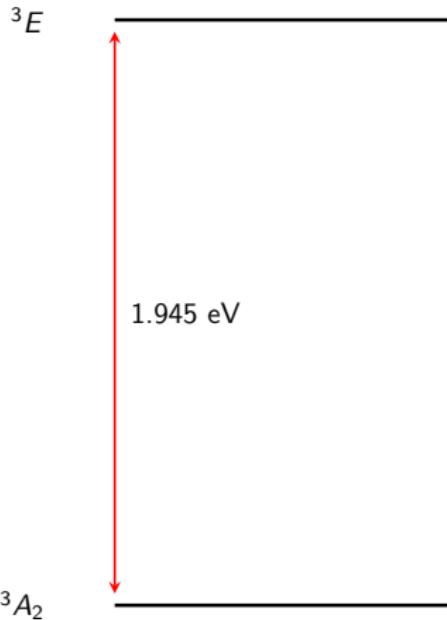
If the whole population is however in the upper x, y states, when radiating, since the non radiative transition to the singlet states is strong,

Transitions overview: NV⁻



- Detection of spin state.
- Realization of a *qubit*.
- Initialization of the state.

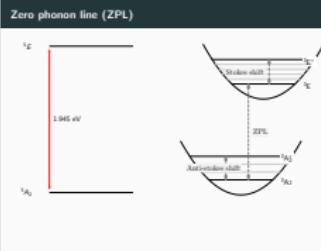
Zero phonon line (ZPL)



Ab initio studies ...

└ Introduction

└ Zero phonon line (ZPL)



To interpret quantitatively some experiments the previous picture falls short in some regards.

Every electronic state is dependent on the ionic constellation. This gives rise to the so-called vibronic states. For example the ground state has associated with it a given ionic constellation. Through excitation to the upper lying triplet state since the dynamic of the electrons is much faster than the ionic one, the constellation first stays static and then relaxes because the potential landscape changed due to the difference in the electronic density.

This gives rise to two different excited states, which must be considered in order to reproduce experimental data.

A very important quantity in this respect is the so-called zero phonon line, which as its name indicates characterizes the position of the

Density functional theory (DFT)

" Ψ contains too much information"

- Popular saying

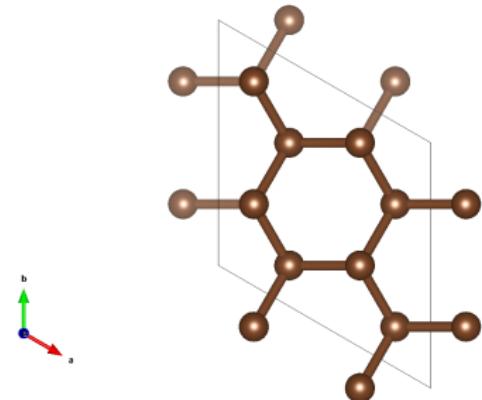
- In principle, DFT delivers the **exact ground state**.
- All quantities are written in terms of ρ (functional formalism).
- E.g.:

$$E[\rho] = T_s[\rho] + \int V(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}^{\text{exact}}[\rho]$$

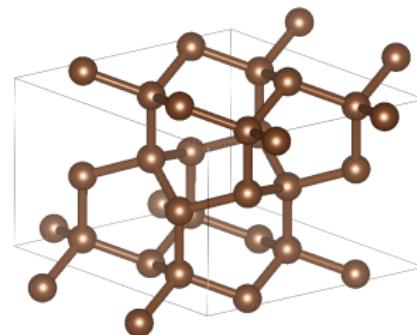
The exchange correlation potential $E_{\text{xc}}^{\text{exact}}[\rho]$ determines the DFT flavor. In many calculations we use the so-called **PBE** (*Perdew-Burke-Ernzerhof*) functional.

Hexagonal diamond and defects

Hexagonal diamond



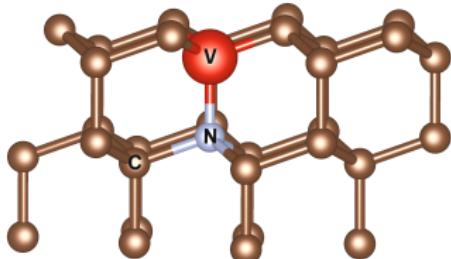
b
a



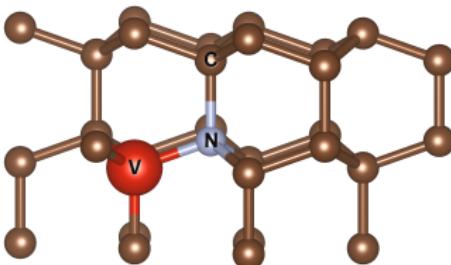
c
b
a

Defected hexagonal diamond

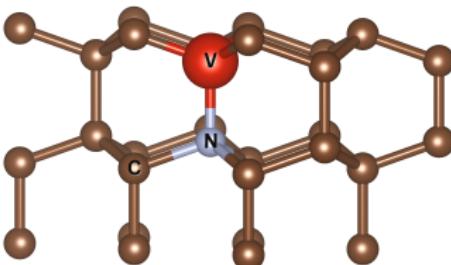
Cubic diamond



Hexagonal x-type

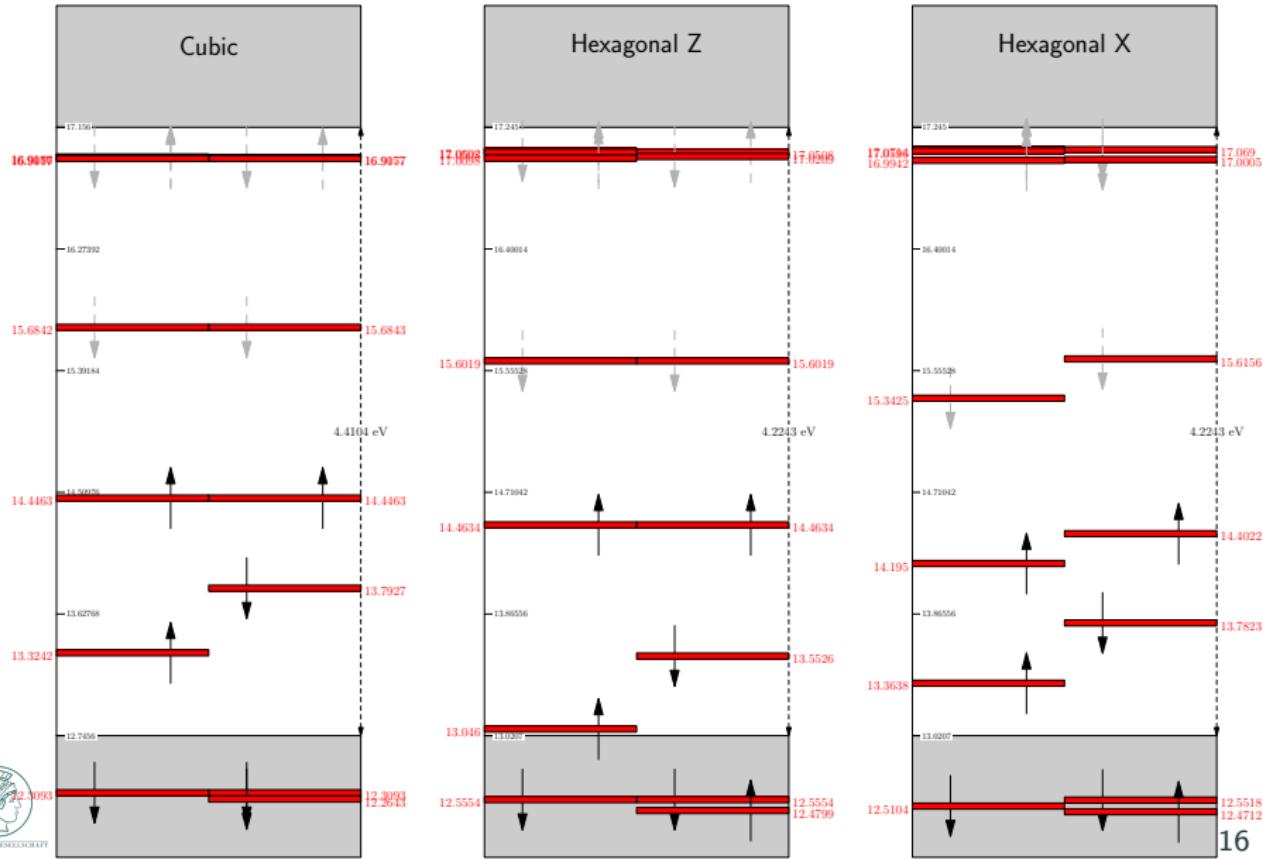


Hexagonal z-type

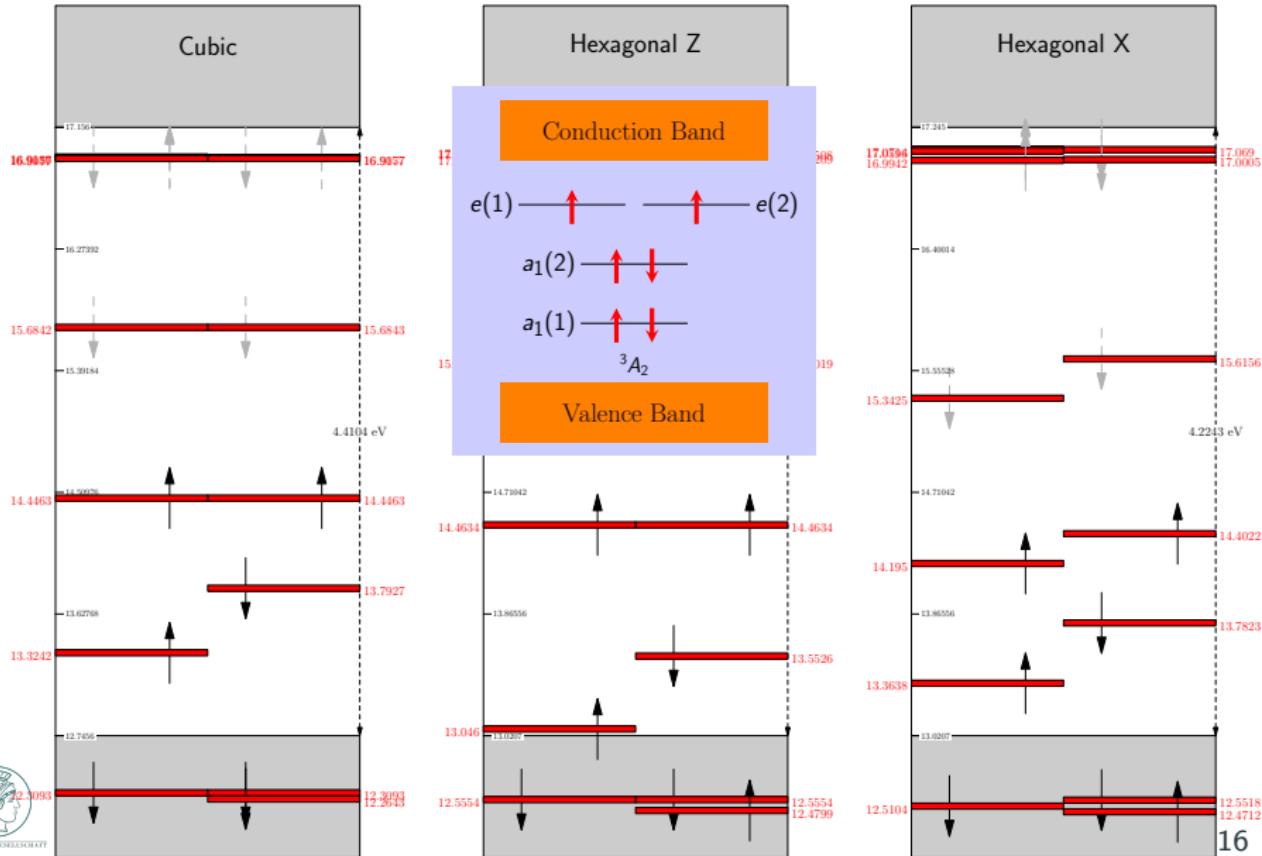


Results

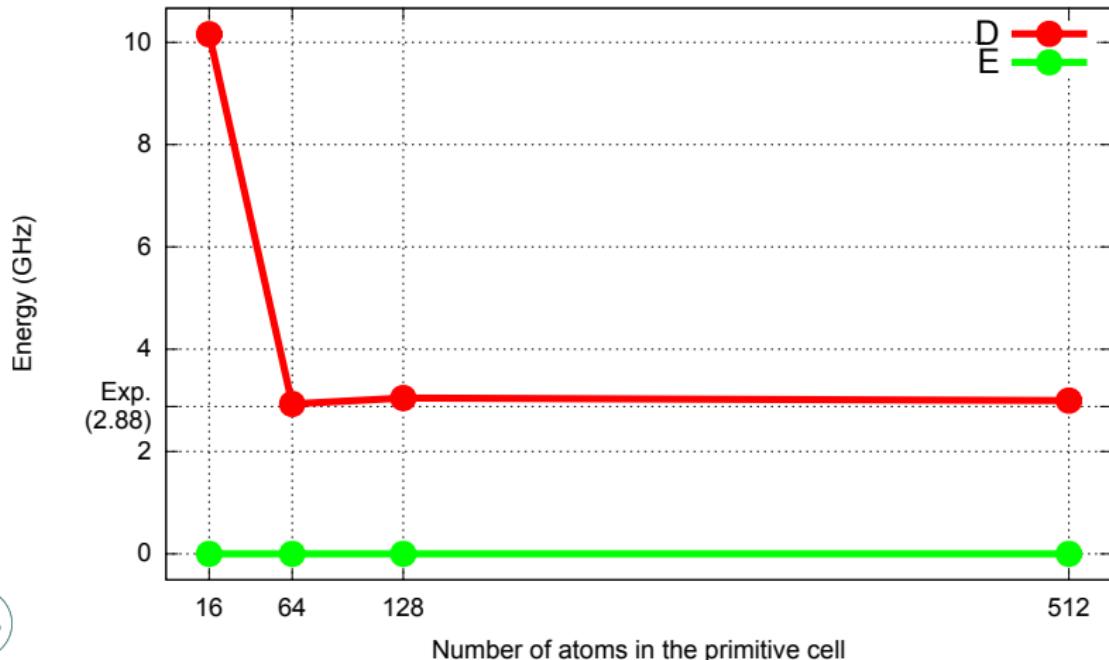
NV⁻: Ground state 3A_2



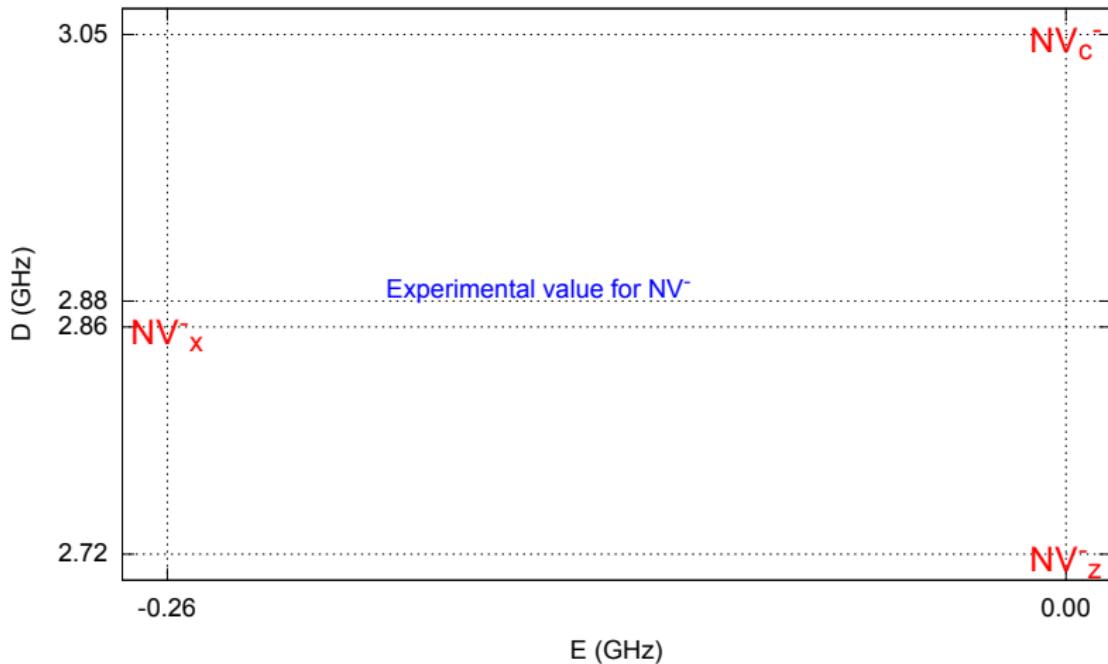
NV⁻: Ground state 3A_2



- Cubic diamond, convergence and comparison with the experimental result.



NV*: ZFS cubic (NV_c^*), Hexagonal x, z ($\text{NV}_{x,z}^*$)



Expanding the defect

18 VIIA							
5	10.811	6	12.011	7	14.007	8	15.999
B	C	N	O	F	Ne		
Boron	Carbon	Nitrogen	Oxygen	Flourine	Neon		
13	26.982	14	28.086	15	30.974	16	32.065
Al	Si	P	S	Cl	Ar		
Aluminium	Silicon	Phosphorus	Sulphur	Chlorine	Argon		
31	69.723	32	72.64	33	74.922	34	78.96
Ga	Ge	As	Se	Br	Kr		
Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton		
49	114.82	50	118.71	51	121.76	52	127.6
In	Sn	Sb	Te	I	Xe		
Indium	Tin	Antimony	Tellurium	Iodine	Xenon		
81	204.38	82	207.2	83	208.98	84	209
Tl	Pb	Bi	Po	At	Rn		
Thallium	Lead	Bismuth	Polonium	Astatine	Radon		
113	284	114	289	115	288	116	293
Uut	Uug	Uup	Uuh	Uus	Uuo		
Ununtrium	Ununquadium	Ununpentium	Ununhexium	Ununseptium	Ununoctium		



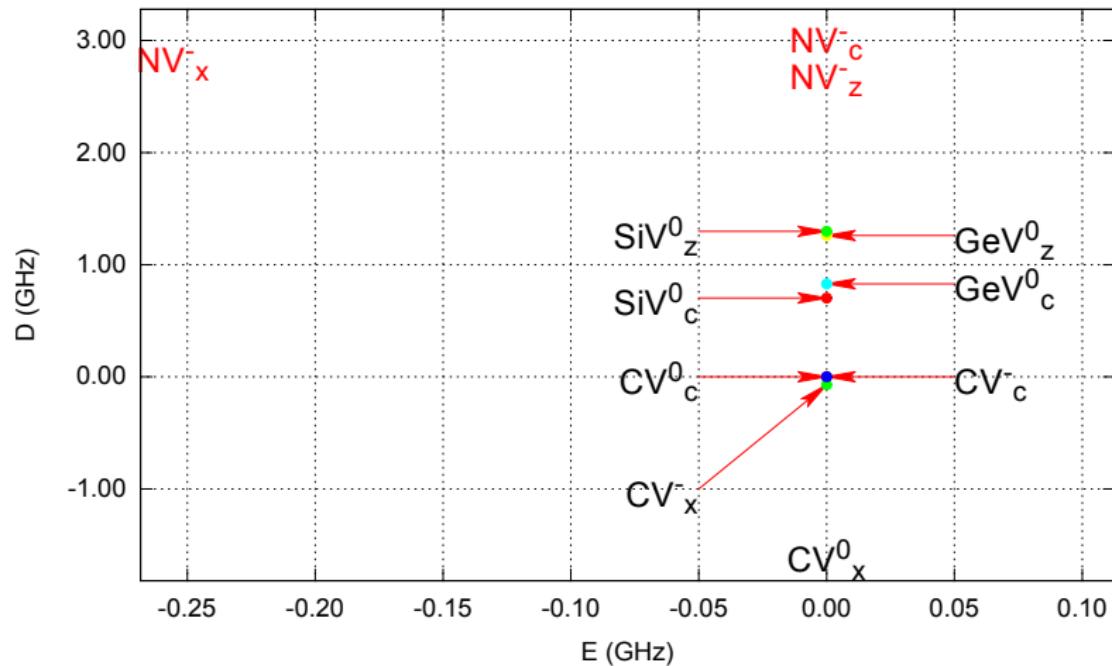
Expanding the defect

14 IVA 15 VA

6 12.011 $\text{CV}_{\textcolor{red}{a}}^q$ Carbon	7 14.007 $\text{NV}_{\textcolor{red}{a}}^q$ Nitrogen
14 28.086 $\text{SiV}_{\textcolor{red}{a}}^q$ Silicon	15 30.974 $\text{PV}_{\textcolor{red}{a}}^q$ Phosphorus
32 72.64 $\text{GeV}_{\textcolor{red}{a}}^q$ Germanium	$a = \{c, x, z\}$ $q = \{+, -, 0\}$



ZFS map



Summary and outlook

Where we are, and where to go next...

- Structural properties
- ZPL calculation.
- ZFS tensor calculation.
- **Beyond the Ground state:**
Using DMRG (*Density Matrix Renormalization Group*) for excited state calculations

Thank you!

